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QUALITATIVE ANALYSIS

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QUALITATIVE ANALYSIS

AS A LABORATORY BASIS FOR THE STUDY OF

GENERAL INORGANIC CHEMISTRY

BY

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PREFACE.

This text presents the course of instruction given by the author to the freshman classes at the University of California where the exigencies of vocational courses render it impracticable for a large number of students to devote more than one year to general inorganic chemistry and to qualitative analysis as well. Therefore, the scheme of qualitative analysis is made to serve as a means of correlating the apparently independent experiments of general chemistry. Thus, while the end in view is primarily the imparting of a knowledge of the general subject, familiarity with analytical methods is obtained. The course presupposes good chemical training in the secondary schools, many of its briefer statements being in the nature of a review rather than of first presentation. No attempt has been made to emasculate the work by eliminating the consideration of more difficult points. On the other hand, the tests for individual elements have been varied in order to familiarize the student with as many significant reactions as possible.

In the opinion of the author, instruction in science should endeavor to equip the student with principles rather than facts and, what is of still greater import, it should train him in the use of these principles and in the application of them in explaining the phenomena of general experience. The acquisition of relatively large numbers of facts or the memorizing of printed rules and laws is a matter of comparatively easy accomplishment. The ability to analyze a situation and to recognize the underlying principle comes less readily. Still more difficult of acquirement is that mental habit which consistently seeks the explanation of the unfamiliar by means of the well-known. In the author's experience, furthermore, students know facts but lack the perspective which gives the appreciation of relative values. Their facts are for the most part individual units, like so many loose beads without any connecting thread by means of which the whole may be viewed as a unit and the relation of the individuals, each to the other, recognized. From certain of the many books at present on the market a good student may *learn* much chemistry; but the author has found it necessary to supply in lecture form the correlating factors and to keep pointing out the application of general principles to cases not less typical than the stereotyped illustration discussed in the text. With the hope of minim-

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izing the necessity for lecture work, the present book appears. By frequent repetition the mind acquires its habits of functioning and becomes thoroughly familiar with its data. By frequent repetition, therefore, the present text endeavors to *teach* the fundamental principles of chemistry and to inculcate the habit of seeking to explain new phenomena, as they occur from time to time, by the methods of past experience. It endeavors to reduce to a rational basis the multitude of chemical reactions, a knowledge of which ofttimes seems to the student to be a mere matter of tedious memorizing.

The method of presentation is based principally, though not exclusively, upon the theory of electrolytic dissociation. Equations are frequently written, first, in the older style expressing whole molecules and afterwards as ionic reactions. This plan conforms to good pedagogical principles by passing from what is known to the student to what is unknown to him. The presentation appears, therefore, as a statement of fact revised and rendered somewhat more complete than the older form with which he is familiar.

In the experience of the author, no difficulty in the presentation of the ionic theory has been encountered. Its essentials seem to be grasped as readily and comprehended as correctly as is any other theoretical conception. No field offers more illustrations of ionic reactions than qualitative analysis. Here the unifying and systematizing value of a fundamental conception seems to be greatly needed. The author would dissent, therefore, from the opinion of those who hold that instruction in qualitative analysis should not be based on the dissociation theory, "however valuable this concept may have proved to chemistry."

The text is divided into four parts. The general principles underlying any intelligent comprehension of the subject are presented briefly in an introductory part. The reactions of individual elements (arranged according to the Periodic System) comprise the second part. The presentation of analytical methods constitutes the third part while several tables of useful information are found in an appendix.

It is hardly necessary to remark that the metric system of weights and measures and the Centigrade scale are used throughout the text. In the analytical section certain abbreviations occur which will be understood without difficulty. The solutions used in the laboratory are of the concentrations given in the appendix. Throughout the text, whenever no concentration is specified, the solutions of acids and alkalies are understood to be the dilute reagents, four times normal.

In the preparation of the text most of the better works on general inorganic chemistry and on qualitative analysis have been consulted freely and statements of fact taken from them. On many points, however, original sources have had to be investigated.

In conclusion, grateful acknowledgment is made of the advice and assistance rendered by several friends who have appreciably lessened the work of publication. In this connection Professor F. C. Cottrell, of the University of California, should be especially mentioned inasmuch as he has had the kindness to read a portion of the original manuscript. Of the constant assistance of my wife in the preparation of the manuscript I would also make mention.

WILLIAM CONGER MORGAN.

BERKELEY, CALIFORNIA,
October, 1906.

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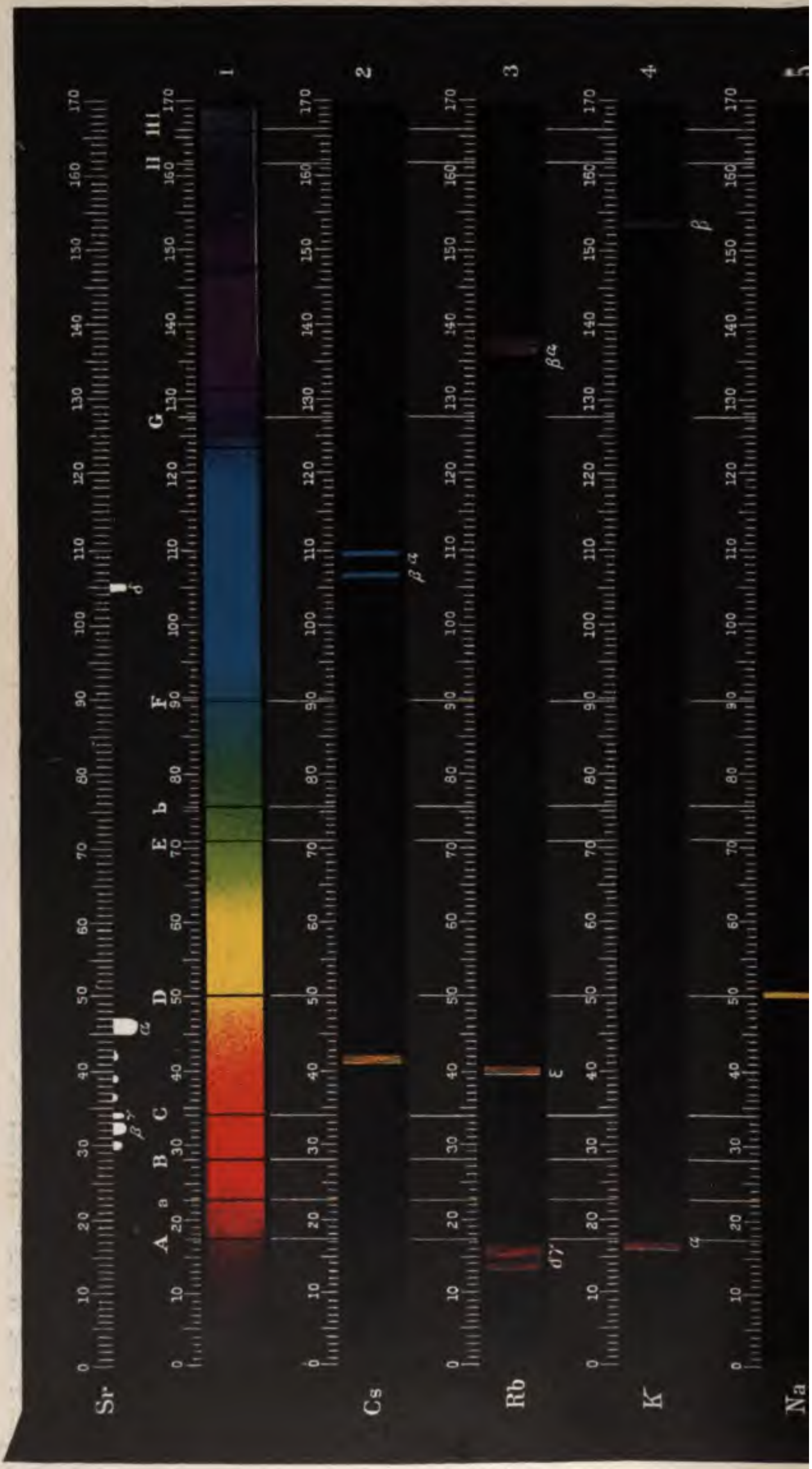
PART I

GENERAL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QUALITATIVE ANALYSIS

Introduction.

Chemistry is that part of natural science treating of the composition of substances. Knowledge of the composition of substances is obtained by three general methods, analysis, synthesis, and metathesis.

Analysis is the taking apart or breaking down of a substance into simpler substances, as:

$$FeS \rightarrow Fe + S \qquad CaCO_3 \rightarrow CaO + CO_2$$

Synthesis is the putting together and building up of more complex compounds, as:

$$Fe + S \rightarrow FeS \qquad CaO + CO_2 \rightarrow CaCO_3$$

Metathesis is a process involving the simultaneous decomposition of two substances and the formation of two new bodies from their components, as:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3{}^*$$

The general term **chemical analysis** includes all those processes of whatever nature by virtue of which we are enabled to ascertain the composition of a body. They are generally of an analytical or metathetical character, but sometimes valuable information is furnished by synthetical methods.

Chemical analysis is divided into two parts, qualitative and quantitative. **Qualitative analysis** is concerned with the kinds of matter composing a given substance without regard to the quantities of the constituents present.

Quantitative analysis determines the proportions in which the constituents are present. A thorough knowledge of qualitative analysis is prerequisite to the satisfactory understanding of quantitative methods.

---

* Throughout the text, hereafter, the physical condition of reagents under the conditions of the experiment will be indicated whenever equations are written. Solids or insoluble substances will be denoted by black-faced type, liquids or substances in solution by ordinary type and gases by italics.

Aside from information as to the composition of the various bodies about us, qualitative analysis affords a very convenient method of coordinating many facts of **general chemistry,** for by a well-arranged series of the apparently independent experiments of general chemistry we are enabled to develop analytical methods. By the frequent laboratory repetition and thoughtful consideration of these processes, the facts of general chemistry become fixed in the mind.

Pure substances possess characteristic properties which are unchanging. Chief among these, for the present purpose, are: physical condition at ordinary temperatures, viz., solid, liquid, or gas; degree of solubility; color; physical structure; specific gravity; melting-point and others of similar nature. By a combination of a sufficient number of properties any substance may be differentiated from all others, and it is by virtue of its properties that we know and recognize each substance. It is important, therefore, to observe carefully and to make a study of the physical properties of the substances with which one comes in contact. It is only by noting the properties of the various products which may be obtained during a qualitative analysis, by comparing these properties with the properties of known substances and realizing their identity or difference that one is able to determine the nature of a body analyzed.

Mixtures do not ordinarily possess characteristic properties by which they may be recognized. While the properties of mixtures are usually a blending of the properties of the constituents, this is not always so. Frequently mixtures do not possess the properties common to the constituents in an average degree, but certain properties are emphasized, others much reduced by the process of mixing. For this reason it is sometimes necessary to separate the constituents of a mixture from each other and obtain each in a state of purity before it can be recognized. This is, however, not usually necessary in qualitative analysis.

Analytical chemistry has so far succeeded in reducing the many varied substances which constitute the world around us into about seventy-five simpler forms of matter, called **elements,** which may be readily differentiated, one from the other. These elements show a remarkable persistence. Most of them unite with other elements to form large numbers of compounds, each one of which possesses entirely distinct properties. By appropriate analytical methods, however, the simple forms may be obtained again and their identity recognized.

Some elements are found widely distributed and in considerable quantities. Others are exceedingly rare. To develop and become familiar with a system of qualitative analysis that should include all the elements would be a task of extreme difficulty. It would be of comparatively little value, moreover, because of the great rarity of nearly one-half of the elementary substances. Hence it is customary to consider only the commoner elements. Those included in the present scheme of analysis have been indicated by black-faced type in the list given on page 324. The letter or letters following each name is the **symbol** by which the element is generally represented.

Qualitative analysis consists in determining primarily what elements are contained in any given substance. Many of the elements are so reactive, however, that they are very rarely found uncombined with others. Furthermore, they are not separated in the free state during the processes of analysis. On the other hand, many combinations of two or more elements, fairly stable under definite conditions, are of frequent occurrence and, since these are well recognized, it is generally not necessary to separate a body into its elementary constituents, but is often sufficient to determine the presence of the **groups,** or **radicles.**

The method of chemical analysis is to change an unknown substance into other substances, the properties and composition of which are well known. From a consideration of the derived substances judgments are formed as to the composition of the original substance. Such a change is known as a **reaction.** It is frequently accomplished by the addition of a substance of known composition and properties called a **reagent.**

Reactions carried on without the presence of appreciable quantities of water are said to be performed in the " **dry way,**" those taking place in aqueous solution in the " **wet way.**"

EQUATIONS.

An **equation** is a chemical short-hand expression of the changes taking place during a reaction, the symbols for the elements and their compounds being used. All the substances which disappear wholly or in part during the reaction are written on one side, while all the substances formed during the reaction are grouped on the other side, separated from the first group by an arrow indicating the direction in which the reaction proceeds, thus:

$$\mathbf{Na + I \rightarrow NaI}$$

For general use the **arrow** is to be preferred to the sign of equality, for the equation is not ordinarily considered as indicating that one side is equal to the other side, but only that one group of reagents passes over into the other.

In writing **formulae** for chemical compounds or equations for reactions the symbol of an element stands for a definite quantity of that element, for one atom* only. Thus H stands for one atom of hydrogen and O for one atom of oxygen. If more than one atom is present, the fact is indicated by a small number written subscript, as H_2. Such a subscript number affects the symbol only which it immediately follows. Thus, H_2O means two atoms of hydrogen and one of oxygen. The formula of a compound expresses the composition of a molecule* of the substance. The symbols of the elements composing it are written together, the proper number of atoms being indicated by subscript numbers, as NaCl, H_2O, and $K_2Cr_2O_7$. If it be desired to indicate more than one molecule of a compound, a large number is prefixed to the formula. This acts as an algebraic coefficient and multiplies each element in the formula. Two molecules of sodium chloride or potassium carbonate are written: 2NaCl and $2K_2CO_3$, and not Na_2Cl_2 or $K_4C_2O_6$.

All **equations should be balanced.** The total amount of matter which appears on one side should be present in some form on the other, the same number of atoms of each element appearing on each side, as is shown in the following equation:

$$2KMnO_4 + 3H_2SO_4 + 10HCl \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10Cl$$

In order to do this it is necessary to resort to quantitative methods and determine the **quantities of the reagents** which enter into a reaction. These determinations have been satisfactorily made and need not be undertaken by the student, but a knowledge of the quantitative relations in any given equation may be ascertained by reference to proper sources or by comparison with the known values in similar reactions.

A chemical equation should be a statement of fact. Before a statement of fact can be made it is necessary to know the facts. Hence it is necessary to know what actually takes place in a given reaction before the equation can be correctly written. Chemical reactions take place for the most part according to well-established laws. A familiarity with these laws and with the nature of chemical elements and compounds will often enable one to tell at a glance from the nature of the substances present and the conditions of the experiment what reaction will take place. It is essential to a good understanding of the subject that the student be able to write equations correctly expressing the changes taking place in the experiments which he is performing. In general the ability to write chemical equations may be taken as an index of the chemical knowledge possessed by the student and of his understanding of the processes which he is performing.

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* For the definitions of the terms atom and molecule see page 8.

AIDS TO CHEMICAL REACTIONS.

Solids do not readily react with each other under ordinary conditions. Liquids and gases are more reactive, however. In order to cause a substance under examination to react, it is frequently necessary to **aid the reaction** by the application of (*a*) mechanical force, (*b*) heat, (*c*) light, (*d*) electricity and (*e*) solution.

(*a*) As an illustration of the action of **mechanical force** it may be stated that potassium chlorate and sulfur, however finely powdered and intimately mixed, will not react. They may be made to unite with explosive violence* by pressure or friction.

(*b*) By the application of **heat** solids ordinarily melt and become liquids. If the temperature be raised still higher, liquids volatilize and become gases.

Aside from the formation of liquids and gases which are more reactive than solids, **heat aids chemical activity** without causing a change in the physical state. Many substances, which, at ordinary temperatures, will not react to any appreciable degree, will do so with the greatest readiness at higher temperatures. A fairly definite relation between the increase in temperature and the time necessary to complete a reaction has been found to exist. As the average result of experimental investigation the general statement may be made that the speed of a reaction is doubled by every increase of 10° Centigrade. Thus by raising the temperature 100° the reaction would be hastened more than a thousand fold, and a reaction which would not take place appreciably during an interval of years at ordinary temperatures might be accomplished in a few minutes at 1000°. Hence it is assumed that all reactions that take place at high temperatures do actually occur at ordinary temperatures, but with a reaction speed which approximates zero. Heat as an agent to hasten chemical activity is of very wide application, and frequently productive of very marked results.

(*c*) To a much smaller degree **light** aids chemical reactions, photochemical action, as it is called, being the foundation of all photographic processes.

---

* Undoubtedly most reactions of this class may be explained as due to the action of heat generated by mechanical force.

(*d*) **Electricity** is sometimes called in to aid a chemical reaction as in the production of pure copper. The crude "matte" is dissolved and the resulting copper sulphate solution electrolyzed with the separation of the metal.

(*e*) A large proportion of all substances known to interact under any conditions will do so readily in solution, especially in aqueous solution. Many of these reactions cannot be made to take place under any other condition. **Solution** in water is, therefore, one of the greatest known aids to chemical activity.

According to present theories, matter is composed of minute particles in constant motion. These **molecules,** as they are called, are defined as *the smallest particles of any substance that can exist and possess the properties of that substance.* Further, each molecule of a compound substance may be divided into the still smaller particles of the elements composing it. When so divided, however, the properties of the compound substance are no longer present, but only the properties of a mixture of elements. *These minute particles of the elementary substances which act as units in the formation of chemical compounds are called* **atoms.** Atoms are supposed to be in constant motion within the molecule.

Heat and light, so far as their nature is known, and possibly electricity, seem to be of a vibratory character. Their action in causing increased chemical activity may easily be explained as the result of a **greater freedom** of motion given to the atoms and molecules. There is, hence, a greater tendency for the molecules to break down and for the atoms to enter into new combinations which are more stable under the conditions present.

The greater freedom of motion of the different parts within a chemical compound thus indicated theoretically may be demonstrated practically. If ammonium chlorid be heated strongly, it breaks down, partially at least, into hydrogen chlorid and ammonia, which may be separated and identified by appropriate means. On lowering the temperature the two parts come together again forming the original substance. Such a decomposition is known as **dissociation.** *A reaction which may go in either direction is said to be reversible.* This is indicated by a double-headed arrow, as in the following equation:

$$\mathbf{NH_4Cl} \leftrightarrow HCl + NH_3$$

DISSOCIATION.

If heat, light and electricity aid chemical activity by increasing the motion within the molecules, it is not improbable that the increased activity of substances in aqueous solution may be explained similarly on the hypothesis of a greater freedom imparted to the components of the molecules. There is abundant evidence to indicate that in solution the dissolved substance exists in a condition so much like the gaseous state that the same laws can be made to apply to a large extent. If dissociation be a phenomenon of the gaseous state may not some similar separation of the components of the molecules take place in solution? There is evidence that such is the case. *Substances whose activity is increased by dissolving them in water dissociate on going into solution.*

The results of the process of **dissociation in aqueous solution** are very analogous to the results of dissociation in the gaseous state. The process, however, seems to be more complex. Evidence is accumulating to indicate that the solvent unites with the components of the molecules after they have dissociated in a way which is not, as yet, clearly understood. In the present considerations it will not be necessary to emphasize this phase of the process since the components of the molecules act in many respects as though they were not associated with the solvent to a degree sufficient to influence chemical reactions.

When common salt dissolves in water, it dissociates more or less completely into minute particles of sodium and chlorin called **ions** and, for the most part, does not exist as molecules in which the metal is united with the non-metallic element. The process is known as **ionization** or **dissociation.**

$$NaCl \rightarrow Na + Cl$$

That these ions, always present in any ordinary salt solution, possess very different properties from metallic sodium and gaseous chlorin must be evident to anyone familiar with these substances. Metallic sodium ordinarily decomposes water, liberating hydrogen and forming sodium hydroxid. Gaseous chlorin normally reacts with water, liberating oxygen, and forms hydrochloric acid. It also readily attacks sodium, forming sodium chlorid, yet the ions of sodium and chlorin exist side by side in solution without appreciable decomposition of the solvent in the usual way.

The difference seems to be due mainly to the fact that **each ion is charged with electricity.** That this is so and that the electrical charge accounts for the difference in properties is indicated by the following facts: Two pieces of platinum may be charged with electricity, the one positively and the other negatively, by being connected with a cell, dynamo or other source of electricity. When so connected they are known as electrodes. If these electrodes be immersed in a solution made by dissolving sodium chlorid in pure water, each loses its charge, although it is a well-known fact that pure water is not an appreciable conductor of electricity. Of course, the charges on the platinum strips are renewed by the cell or dynamo and, by suitably modifying the apparatus, sodium may be collected on one electrode while chlorin is liberated on the other.

The explanation seems to be as follows: The sodium ions are attracted to the electrode charged with negative electricity because they carry a positive charge of electricity. At any rate, they leave the solution entirely and deposit on the electrode, which loses its charge of negative electricity exactly as if neutralized by the addition of plus electricity. But as soon as the sodium ions give up their charges, they take on all the properties of metallic sodium and, unless protected from the action of the water, they react with it in the usual way.

Similarly the chlorin ions, being negatively charged, deposit on the positively charged electrode. They give up their electricity, cease to be ions, and assume all the properties of gaseous chlorin. In this way the process of **electrolysis,** or *analysis by means of an electric current,* is explained. *No solution will conduct an electric current that does not contain ions.* This decomposition, by virtue of which electrolysis becomes possible, is sometimes called electrolytic dissociation, and the substance that dissociates, the **electrolyte.**

The ions formed by the metals and by hydrogen are charged with plus electricity and in electrolysis go to the kathode or negative electrode. They are called kathions. Non-metallic ions, charged with minus electricity, go to the anode or positive electrode and are called anions.

The **degree of dissociation** increases as the dilution increases. The greater the volume of water in which a given amount of a substance is dissolved, the more completely will it be ionized. Conversely, by decreasing the volume of the solvent, dissociation is lessened, for the ions come together to form undissociated substance.

It may be demonstrated readily that no electricity passes off with the vapors of the solvent upon evaporation. If a salt solution, completely dissociated into sodium and chlorin ions charged with electricity of opposite sign, be evaporated without loss of electricity, it leaves an electrically neutral solid. The quantity of electricity on the sodium ions must be equal, therefore, to the quantity of electricity on the chlorin ions. Since the number of the two kinds of ions is equal, the charge on each sodium ion must be equal in quantity, though of opposite sign, to the charge on each chlorin ion. In this way it may be demonstrated that **the amount of electricity on kathions of any kind is equal to the charge on the anions produced with them.**

In a solution of calcium chlorid, however, there are two chlorin ions for one calcium ion. It follows, then, that each calcium ion carries twice the charge on each chlorin ion, or twice the charge on each sodium ion. *The amount of electricity carried by each sodium or chlorin ion is taken as the unit charge.* The calcium ion, therefore, carries two unit charges.

The separation of equal amounts of opposite electricity is an essential factor in the dissociation of any substance, and is usually indicated by the use of plus (+) and minus (—) signs written above the symbol for the kathion or anion, one sign being affixed for each unit charge of electricity on the ion. The reaction for the ionization of sodium chlorid may be more correctly written as follows:

$$\mathrm{NaCl} \leftrightarrow \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}}$$

Similarly for calcium chlorid:

$$\mathrm{CaCl_2} \leftrightarrow \overset{++}{\mathrm{Ca}} + 2\overset{-}{\mathrm{Cl}}$$

By anology one would say:

$$\mathrm{FeCl_3} \leftrightarrow \overset{+++}{\mathrm{Fe}} + 3\overset{-}{\mathrm{Cl}}$$

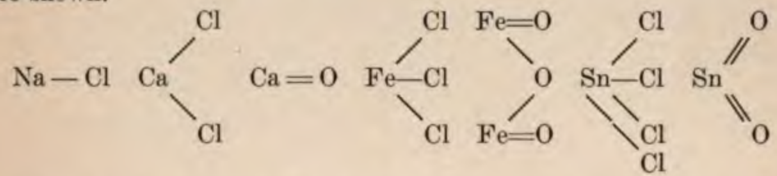
and

$$\mathrm{SnCl_4} \leftrightarrow \overset{++++}{\mathrm{Sn}} + 4\overset{-}{\mathrm{Cl}}$$

Ions carrying one unit charge are called **univalent**; *ions with two charges,* **divalent**; *three charges,* **trivalent**; *and four charges,* **tetravalent.** While univalent and divalent kathions are of frequent occurrence, trivalent kathions are less common, and tetravalent kathions are but little known. Elementary anions with a valence of more than two are unknown. (See page 13.) As the valence rises, the tendency toward ion formation decreases while other influences tending to remove ions from solution increase. (See page 46.)

On evaporation of a solution containing various ions, two univalent anions unite with one divalent kathion to form a solid. Similarly, three univalent ions unite with one trivalent ion oppositely charged, and four univalent ions with one tetravalent ion. Two divalent ions unite with one tetravalent ion and three divalent ions with two trivalent ions. Consequently the idea of **valence** is extended from ions in solution to substances out of solution whether they may ionize or not. *A univalent element is one which will form univalent ions or will unite with elements forming univalent ions, atom for atom.* A divalent element is one which will form divalent ions or will unite with elements forming divalent ions, atom for atom. Trivalent and tetravalent elements are similarly define.

In writing the formulae for compounds which are not represented in the ionic condition, the valence of each element may be indicated by **bonds** joining the different elements together, one bond for each valence shown.



Sodium and chlorin are here indicated as univalent elements, calcium and oxygen as divalent elements, iron trivalent, and tin tetravalent. The valences ordinarily shown by the elements as they are encountered in qualitative analysis are given on page 324. Under varying conditions the valence of an element may change. This point will be considered later. (See page 45.)

Ions need not necessarily be elementary in character, but are often of a compound nature consisting of a group or radicle acting as a unit, as the following dissociation equations indicate:

$$Na_2CO_3 \rightarrow 2\overset{+}{Na} + C\overset{=}{O}_3 \qquad Ca(NO_3)_2 \rightarrow \overset{++}{Ca} + 2N\overset{-}{O}_3$$

$$(NH_4)_2SO_4 \rightarrow 2\overset{+}{N}H_4 + S\overset{=}{O}_4$$

Ions of a still more complex nature may be formed by definite chemical reactions between two different simple ions or between a simple ion and an undissociated substance. The silver ion, $\overset{+}{Ag}$, unites directly with ammonia to form a complex ion, $\overset{+}{Ag}(NH_3)_2$, which possesses properties entirely different from the simple silver ion. The cyanid ion, $\overset{-}{C}N$, unites in an analogous way with silver cyanid, $AgCN$, to form a new ion, $Ag(\overset{-}{C}N)_2$, in which the metal, silver, constitutes a part of the negatively charged anion instead of acting as a simple positively charged kathion. Ammonia and cyanogen compounds show especial tendencies to the formation of complex ions.

Complex ions vary very greatly in the readiness with which they are formed and in stability after being formed. In order to produce certain ones it is only necessary to bring together the reagents necessary to form them when an immediate reaction takes place. In other cases it is necessary to aid the reactions in various ways. There is always a tendency for complex ions to decompose into simpler ones. Because of this certain solutions contain a mixture of simple and complex ions. In other cases the stability of the complex ion is so great that no appreciable amount of the simple ions can be detected.

Complex anions with a valence of three and four are met with in qualitative analysis. (See page 11.)

Water is the only one of the common **solvents causing dissociation** to any great extent, although acetic acid and alcohol have slight dissociating properties. Many less common solvents, such as liquid hydrogen cyanid, sulfur dioxid and ammonia, and many fused salts, cause dissociation to a high degree.

All substances are not dissociated in water solutions. Many of the compounds of carbon with hydrogen and other elements, known as organic compounds, do not dissociate at all. On the other hand, most of the soluble mineral or **inorganic substances are dissociated.** These are the substances with which qualitative analysis is chiefly concerned.

This fact greatly simplifies qualitative analysis. Each soluble salt of a given metal with the various acids gives the same kathion. Similarly, each soluble salt of a given acid with the various metals gives the same anion. It makes no difference whether calcium nitrate, chlorid, acetate, or bromid is used; any soluble calcium salt will give the same kathion. It is a characteristic of the calcium ion that it gives a white precipitate with a solution of sodium carbonate, or with the solution of any other soluble carbonate containing the carbonate ion in appreciable quantities. Hence it is not necessary to learn the reaction of calcium chlorid on sodium carbonate, of calcium nitrate on ammonium carbonate and of calcium sulfate on potassium carbonate, but simply to **study the various ions** and learn the characteristic reactions of each.

The reactions used in qualitative analysis are almost entirely **reactions between ions.** This is well illustrated by the following facts: It is loosely stated that silver nitrate is a reagent for chlorin, forming with it an insoluble white compound. *Silver nitrate is a reagent for the chlorin ion only.* Most organic compounds containing chlorin, even chloroform which is almost ninety per cent. chlorin, give no precipitate with silver nitrate because they do not dissociate. Chlorates and perchlorates, although they ionize readily, give no precipitate because the ions formed are $\mathrm{C\overline{l}O_3}$ and $\mathrm{C\overline{l}O_4}$ and not the simple $\mathrm{\overline{Cl}}$. Free chlorin gives not a trace of a precipitate as long as it remains un-ionized. On the other hand, every substance that dissociates into $\mathrm{\overline{Cl}}$ ions gives an abundant precipitate. Thus there is ample evidence that it is the chlorin ion alone that reacts with silver nitrate. More correctly speaking, it is the silver ion, $\overset{+}{\mathrm{Ag}}$, and not silver nitrate that reacts with the $\mathrm{\overline{Cl}}$ ion, for undissociated silver nitrate does not react, neither will the ions $\mathrm{Ag(\overset{+}{N}H_3)_2}$ or $\mathrm{Ag(C\overline{N})_2}$ or any other complex ion containing silver. Any compound forming the simple silver ion will react, however. Since silver nitrate is the only common silver compound readily soluble, it is almost universally used to introduce the silver ion, and, hence, silver nitrate is often mentioned when the silver ion is really meant.

Dissociation is the characteristic phenomenon of dilute solutions. In concentrated solutions, not only is dissociation reduced, but substances tend to associate or come together in various ways. The principles and laws which hold for dilute solutions are only partially true for concentrated solutions and a different set of phenomena are to be observed. One of the most important types of association is the formation of **double salts,** such as the double sulfates of aluminum (and certain other trivalent metals) with the alkali metals. As a typical illustration ordinary alum, $\mathrm{KAl(SO_4)_2}$, or as the formula is often written, $\mathrm{K_2SO_4.Al_2(SO_4)_3}$, may be taken. In a dilute solution containing the sulfates of potassium and of aluminum, only simple ions such as $\overset{+}{\mathrm{K}}$, $\overset{+++}{\mathrm{Al}}$ and $\mathrm{S\overline{O}_4}$ are present. As the solution concentrates, these ions come together to form the undissociated sulfates and, on further evaporation of the solvent, these simple salts unite to form the double salt which crystallizes out.

Double salts are to be regarded as salts of complex acids dissociating primarily into complex anions which, being very unstable, break down into simple ions as soon as the dilution becomes sufficiently great to allow ionization to become the dominant phenomenon. The more stable of the double salts are those whose anions do not decompose into simple ions readily but which even in dilute solutions give characteristic complex ions. The double cyanids of iron with other metals are of this kind. (See page 223.)

The following equation will serve to make clear the way in which a double salt dissociates:

$$\mathrm{KAl(SO_4)_2} \leftrightarrow \overset{+}{\mathrm{K}} + \mathrm{Al(\overline{S}O_4)_2} \leftrightarrow \overset{+}{\mathrm{K}} + \overset{+++}{\mathrm{Al}} + 2\mathrm{S\overline{O}_4}$$

The complex ion, $\mathrm{Al}(\bar{\mathrm{S}}\mathrm{O}_4)_2$, is not known with certainty and possibly has only a momentary existence but all degrees of stability from this up to the most stable are well recognized.

ACIDS, BASES AND SALTS.

A study of the various chemical compounds has revealed the fact that many substances, apparently differing as widely in chemical nature as they do in composition, possess certain common properties. The substances, HCl, H_2SO_4, HNO_3, $H_4C_2O_2$, and many other compounds having very different formulae are all characterized by the possession of a sour taste, the ability to dissolve zinc and other metals and the power of affecting certain organic dyes in a uniform way, as, for instance, turning blue litmus red, red phenolphtalein white and yellow methyl orange red. Because of their acid taste, these substances are called acids. Science seeks to find a **common cause for a common phenomenon.** The only common factor present in each of these compounds is hydrogen.

On the other hand, a great number of organic compounds contain hydrogen but do not exhibit these properties. The hydrogen, therefore, must be present in two different conditions in the two different classes of bodies. In short, the *hydrogen present in* **acids** *exists in the ionic condition.*

To the presence of hydrogen ions all acid properties are due, and since ions exist only in solution, it follows, strictly speaking, that acid properties are to be found only in solution. That this is true is indicated strongly by the facts that hydrogen chlorid, HCl, and hydrogen sulfate, H_2SO_4, lose their acid properties so decidedly as they are separated more and more completely from water that the conclusion seems evident that were it possible to obtain these substances perfectly free from water, they would possess absolutely no acid properties. The addition of water, however, causes the appearance of acid properties in a marked degree. *An acid* may be defined as *any substance which in the presence of water will dissociate into hydrogen ions.*

The hydroxids of certain elements act in this way and separate hydrogen ions in aqueous solution. The elements from which they are derived are known as **non-metallic** or **acidic,** *i. e.,* acid-forming **elements.** The hydrids of some of these same elements possess acid properties.

The readiness with which the various acids separate hydrogen ions and, consequently, the degree to which they are present in solutions varies greatly and constitutes the difference between **strong and weak acids.** *That acid is strongest which* is most completely dissociated.

In solutions of such strength as is suitable for qualitative analysis reactions the following acids are more than **three-quarters dissociated** into their respective ions. They are, therefore, very strong acids:

Hydriodic
Hydrobromic
Hydrochloric
Chloric
Perchloric
Permanganic
Nitric
Thiocyanic
Tetrathionic

At the same dilution the following acids are about **one-half dissociated:**

Sulfuric
Dichromic
Ferrocyanic
Silicofluoric
Ferricyanic
Oxalic—about 25 per cent.

Under the same conditions the following acids are dissociated less than **ten per cent:**

Sulfurous
Phosphoric
Arsenic
Hydrofluoric
Nitrous
Tartaric
Acetic

None of the following acids are dissociated as much as **one per cent.** in ordinary solutions:

Carbonic
Hypochlorous
Arsenious
Hydrosulfuric
Hydrocyanic
Boric
Silicic

In dilute solutions of strong acids the dissociation is practically complete. When a **metal** is **added to an acid** in dilute solution, as, for instance, zinc and hydrochloric acid, each $\overset{+}{H}$ ion gives up its plus charge to the metal which then passes into the ionic condition while the hydrogen escapes as gas, as the following equation indicates:

$$\mathbf{Zn} + 2\overset{+}{\mathrm{H}} + 2\overset{-}{\mathrm{Cl}} \rightarrow \overset{++}{\mathrm{Zn}} + 2\overset{-}{\mathrm{Cl}} + H_2$$

Thus the hydrogen in an acid is capable of being replaced by a metal. There remains in solution the same number of $\overset{-}{\mathrm{Cl}}$ ions as before the reaction. Since they appear on both sides of the equation, they may be stricken out and the equation simplified as follows:

$$\mathbf{Zn} + 2\overset{+}{\mathrm{H}} \rightarrow \overset{++}{\mathrm{Zn}} + H_2$$

Thus it is that hydrogen is driven out of the acid because of the greater tendency of the zinc to pass into the ionic condition.* In place of hydrogen ions there exist in solution zinc ions which, on evaporation of the solution, unite with the chlorin ions to form zinc chlorid.

In hydrochloric acid, HCl, there is one part of hydrogen to one of chlorin; in nitric acid, HNO_3, one part of hydrogen to one of the group NO_3; in sulfuric acid, H_2SO_4, two parts of hydrogen to one of the radicle SO_4; in phosphoric acid, H_3PO_4, three parts of hydrogen to one of the radicle PO_4 and in silicic acid, H_4SiO_4, four parts of hydrogen to one part of the group SiO_4. In these compounds, theoretically at least, all of the **hydrogen is capable of passing into the ionic state and of being replaced by a metal** in the formation of salts. On the other hand, in acetic acid, $H_4C_2O_3$, only one part of hydrogen is capable of passing into the ionic condition; in tartaric acid, $H_6C_4O_6$, two parts and in citric acid, $H_8C_6O_7$, only three parts. Hence it is obvious that all of the hydrogen in a compound may not be capable of passing into the ionic condition and of conferring acid properties on its solutions.

Acids are classified according to the amount of hydrogen which may become ionic. Regarding them from the molecular standpoint, if from one molecule of a substance one atom of hydrogen may pass into the ionic condition and be replaced by a metal in the formation of salts, the compound is said to be a **monobasic** acid. **Dibasic, tribasic** and **tetrabasic acids** separate two, three and four hydrogen ions from one molecule of the substance and are known as polybasic acids. It is customary to indicate that part of the hydrogen in a compound which is capable of forming hydrogen ions. In a formula, it is usually written first, separated from the rest of the hydrogen in such a compound, acetic acid being written $H(C_2H_3O_2)$ and tartaric acid $H_2(C_4H_4O_6)$. In the dissociation of such acids that part of the hydrogen which does not form the kathion remains united with the other elements in a group which becomes the anion.

All of the hydrogen in a **polybasic acid** does not pass at the same time into the ionic condition. The dissociation takes place step by step and the process of separating one hydrogen ion from each molecule of acid present is generally pretty well advanced before the separation of a second hydrogen ion from any molecule begins. The dissociation of a third and fourth ion from the same molecule is correspondingly tardy. In dilute solutions of strong acids, such as the dibasic sulfuric acid, the dissociation according to both steps is practically complete and the prevalent anion contains no hydrogen, as the following equations will indicate:

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* The varying tendency of elementary substances to take on the electrical charge and pass into the ionic condition is shown by the table known as the Potential Series given on page 327. In this table the elements are arranged in regular series beginning with those which pass most rapidly into the ionic condition. As in the case of zinc and the hydrogen ion, if a free element comes in contact with the ions of another element standing much lower in the Potential Series, the charge passes from the one to the other and the former goes into the ionic condition while the latter is thrown out in the free state. Many illustrations of this principle will be noted in the second part of this book.

$$\left.\begin{array}{l} H_2SO_4 \rightarrow \overset{+}{H} + H\overset{-}{SO_4} \\ H\overset{-}{SO_4} \rightarrow \overset{+}{H} + \overset{=}{SO_4} \end{array}\right\} = 2\overset{+}{H} + \overset{=}{SO_4}$$

With weak acids dissociation of all the hydrogen present in any one molecule remains to a considerable degree unaccomplished even in dilute solutions. Thus the tribasic phosphoric acid separates ions according to the first and second of the following reactions, but the hydrogen-free anion formed according to the third reaction is present in solution to only a small amount:

$$\begin{array}{c} H_3PO_4 \rightarrow \overset{+}{H} + H_2\overset{-}{PO_4} \\ H_2\overset{-}{PO_4} \rightarrow \overset{+}{H} + H\overset{=}{PO_4} \\ H\overset{=}{PO_4} \rightarrow \overset{+}{H} + \overset{\equiv}{PO_4} \end{array}$$

Analogous to the acids there exists a group of the hydroxids of **metallic elements** which possess the common properties of destroying acids, of turning litmus blue and of affecting other organic dyes uniformly. These compounds differ in their composition and are alike only in that they *form hydroxyl ions,* $\overset{-}{OH}$*, in solution. These substances are known as* **bases,** *since by neutralizing the various acids, with each hydroxid as a base, a series of compounds, known as salts, results.* With the bases as with the acids, the degree of dissociation determines the strength.

In solutions of the strength ordinarily used in qualitative analysis, sodium and potassium hydroxids are more than **three-quarters dissociated,** and, therefore, are very strong bases.

Barium hydroxid is about **one-half dissociated.** Strontium, calcium and magnesium hydroxids are much less soluble, but to the extent to which they dissolve, they dissociate approximately to the same degree as barium hydroxid at the same dilution. As bases, therefore, they are of about the same strength.

Ammonium and silver hydroxid are dissociated **less than ten per cent.**

The hydroxids of the other metals are very insoluble and act as **very weak bases,** *trivalent hydroxids being generally weaker than divalent hydroxids.*

When an acid and a base are mixed together in the proper proportions the one is said to neutralize the other, for the resulting solution possesses neither acidic nor basic properties. On treating a dilute solution of hydrochloric acid with a dilute solution of sodium hydroxid, such a reaction takes place and the acid is neutralized by the base. This reaction is often written:

$$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

In dilute solutions, however, hydrochloric acid, being a strong acid, and sodium hydroxid, being a strong base, are dissociated to practical completion. Sodium chlorid is almost completely ionized at the same dilution. Hence the reaction may be more correctly written:

$$\overset{+}{\text{Na}} + \overset{-}{\text{Cl}} + \overset{+}{\text{H}} + \overset{-}{\text{OH}} \rightarrow \overset{+}{\text{Na}} + \overset{-}{\text{Cl}} + \text{H}_2\text{O}$$

After mixing, the sodium and chlorin are present in the ionic condition exactly as they were in the two original solutions. Since they appear on both sides of the equation, they may be stricken out and the equation simplified as follows:

$$\overset{-}{\text{OH}} + \overset{+}{\text{H}} \rightarrow \text{HOH}$$

The only product actually formed on mixing the solutions is water. Since all acid solutions owe their properties to the presence of the hydrogen ions while basic solutions owe their properties to the presence of hydroxyl ions, *the* **neutralization of** (dilute solutions of) **strong acids with strong bases** *is essentially the formation of water from its ions.*

To speak of the formation of a salt in this process is, therefore, technically incorrect since no reaction takes place to form it, except on evaporation of the solution when the ions come together. That this is true is indicated by the fact that when equivalent amounts of fully dissociated solutions of any acid and base are mixed, the amount of heat liberated is always the same. When any compound is formed, a definite amount of heat enters the reaction which is known as the heat of formation. This is, in general, different for every compound. Hence, if different salts were actually formed by mixing dilute solutions of sulfuric, nitric, and hydrochloric acids with dilute solutions of sodium, potassium and calcium hydroxids, the **heats of neutralization** could not be the same. On the other hand, if one product only, *i. e.*, water, is formed by mixing these different reagents, we should expect the same amount of heat to be liberated in each case. By the formation of water from its ions all hydrogen and hydroxyl ions are removed and all acid and basic properties disappear. There is left a solution containing the ions characteristic of a salt. Since by evaporation of the solution a salt is actually formed, it is ordinarily stated that the neutralization of an acid with a base forms a salt.

Of the three typical methods of **salt formation**: (*a*) by the *action of an acid on a metal*, (*b*) by the *neutralization of an acid with a base*, (*c*) by the *action of an acid on a metallic oxid*, two have already been considered. The third method is a process in which the charges on the hydrogen ions are transferred to a metallic kathion in a manner similar to the interaction of hydrogen ions and metals. After passing out of the ionic condition the hydrogen is not set free, however, but unites with the oxygen of the oxid to form water. A typical reaction will make clear the changes that take place.

$$CaO + 2\overset{+}{H} \rightarrow \overset{++}{Ca} + H_2O$$

It is not essential that all of the hydrogen and oxygen contained in a base be capable of forming $\overset{-}{OH}$ ions. As with acids, so with bases. A substance capable of forming one $\overset{-}{OH}$ ion from one molecule of the compound is called a **monoacid base** since in the formation of salts this $\overset{-}{OH}$ ion is replaced by a single anion of a monobasic acid. **Di, tri,** and **tetracid bases** are capable of separating, theoretically at least, two, three and four $\overset{-}{OH}$ ions from one molecule of the compound.

One molecule of a monacid base will neutralize one molecule of a monobasic acid. Four molecules of a monobasic acid will react with one molecule of a tetracid base. Two molecules of a tribasic acid will unite with three molecules of a diacid base and vice versa. Polyacid bases dissociate step by step in a manner exactly like the ionization of polybasic acids. (See page 18.)

While there is the greatest variation in the degree of dissociation of the various acids and bases, most **salts ionize freely.*** Even the salts of weak acids and weak bases dissociate readily. In this case, however, other factors enter into the consideration and complicate the result. (See pages 28–30.)

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* Salts may be divided according to a classification based on the acids and bases from which they are derived and the variation in the degree of dissociation for salts may be stated for each of these types.

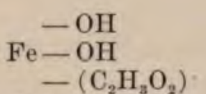
Salts formed by the interaction of monobasic acids and monoacidic bases dissociate almost as readily as the strongest acids and bases.

Salts formed from a dibasic acid and a monoacidic base or vice versa are somewhat more than half dissociated at ordinary dilutions.

Salts derived from dibasic acids and diacid bases are somewhat less than half dissociated under the same conditions.

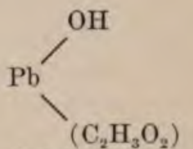
With salts derived from tri- and tetrabasic acids and tri- and tetra-acidic bases other phenomena often play more important parts than dissociation. (See pages 28–30, also 46.)

Acids may be designated as those substances which *separate hydrogen as kathion. Bases separate hydroxyl as anion. Salts separate kathions other than hydrogen and anions other than hydroxyl.* Many substances are known, however, which, in solution, separate both hydroxyl and other non-metallic anions at the same time. These are evidently mixtures of the ions characteristic of bases and of salts. In some instances possibly no serious objection can be raised to considering such substances as very intimate mixtures of the base with one of its salts. In other cases the mixture seems to be inside the molecule. Each individual molecule seems to possess the properties of both base and salt. The substances act as though they were in no ordinary sense mixtures, since they cannot by any means be separated into the pure salt and the pure base. On further treatment with acids they lose their basic properties entirely. For these reasons they are believed to be *salts in which part only of the hydroxyl which is characteristic of the base has been replaced by an acid anion.* They *are called* **basic salts,** therefore, and the formulae indicate their apparent constitution.



$$\mathrm{Fe}\begin{array}{l}-\mathrm{OH}\\-\mathrm{OH}\\-(\mathrm{C_2H_3O_2})\end{array}$$

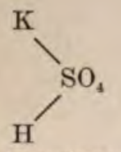
Basic ferric acetate.



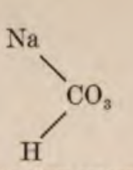
Basic lead acetate.

Analogously, certain other substances separate at the same time hydrogen and other metallic kathions. For similar reasons they are known as **acid salts.** Since the proportion of salt to the acid is far more constant than the proportion of salt to base in basic salts, there hardly seems reason for considering any well-characterized acid salt as a mere mixture of an acid with one of its salts. The following formulae indicate the apparent constitution of typical acid salts.

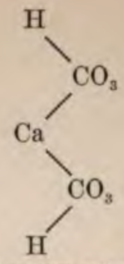
Certain exceptions to this general statement are well known. The halogen compounds of mercury ionize to a very slight degree, those of cadmium somewhat more while the zinc halids together with lead and certain other acetates stand intermediate between these and other salts.



Acid potassium sulfate.



Acid sodium carbonate.



Acid calcium carbonate.

Acid salts are frequently indicated by the prefix "bi," as potassium bisulfate, sodium bicarbonate, etc.

To distinguish acid and basic salts from the type which separates only kathions other than hydrogen and anions other than hydroxyl, members of this latter class are called **normal salts.**

Acid salts are usually far more soluble, basic salts far less soluble, than the corresponding normal salts.

Certain bodies are capable of dissociating in more than one way. The hydroxids of elements which have neither a pronounced metallic nor non-metallic character may separate under one condition hydrogen ions and under another condition hydroxyl ions. Arsenic, antimony, tin, lead, zinc and aluminum are elements of this nature and their **hydroxids may act either as acids or bases.** To illustrate: zinc hydroxid, ZnO_2H_2, may dissociate into $\overset{++}{Zn}$ and $\overset{-}{OH}$ ions in which case the positively charged zinc ions are acting as metallic ions. Zinc hydroxid may separate $\overset{+}{H}$ ions and $Z\overset{=}{n}O_2$ ions in which case the negatively charged anion shows zinc to be playing the part of an acid-forming element. In acid solutions zinc hydroxid separates $\overset{-}{OH}$ ions which unite with the $\overset{+}{H}$ ions furnished by the acid to form undissociated water and leave in solution ions of a salt, such as zinc chlorid, $ZnCl_2$. In solutions containing hydroxyl ions in quantity, zinc hydroxid separates $\overset{+}{H}$ ions. The hydrogen and hydroxyl ions unite to form water and leave in solution sodium zincate, Na_2ZnO_2, or other salt in which zinc acts as an acid-forming element.

EQUILIBRIUM AND MASS ACTION.

If the metathesis $AX + BY \leftrightarrow AY + BX$ be a reversible reaction, when AX and BY are brought together, they will react to form AY and BX with a definite reaction speed. At the end of the first short period during which the reaction has run there will exist an intimate mixture of four substances of which AX and BY will be present in much greater proportion than AY and BX. AY and BX as soon as formed will react together to form AX and BY again, but, other things being equal, more of AY and BX will be formed in any given interval by the original metathesis than of AX and BY by the second reaction, because of the simple fact that there is so much more of AX and BY to interact than there is of AY and BX. The first reaction will continue to predominate until all four substances are present in certain definite proportions. Then we may consider each reaction as taking place at the same time and to such a degree that the proportions of the constituents remain unchanged.

If, now, more of AX and BY be added, the original reaction will again become dominant until the same proportion among the constituents is reached.

Such *a condition which, when disturbed, tends to restore itself is known as* **equilibrium,** and the reaction by which it is restored as the equilibrium reaction.

Such is the nature of the process which is going on whenever a chemical reaction takes place. That **reactions are reversible** generally is believed to be true. The fact that many reactions do not seem to be reversible in practice is due to the presence of determining factors which shift the equilibrium, from the condition of, possibly, equal proportions among the constituents to a condition in which some constituents are practically absent.

To consider a particular reaction: If ethyl hydroxid (*i. e.*, ordinary alcohol) and acetic acid be heated together, a reaction takes place in part, leading to the formation of ethyl acetate and water. Equilibrium is soon reached in which the four substances, alcohol, acetic acid, ethyl acetate and water are present in proportions which are influenced by temperature, but which are definite for any given temperature. On the other hand, if ethyl acetate and water are heated together, a partial reaction ensues leading to the formation of some alcohol and acetic acid. Equilibrium ensues, a mixture of the four substances being formed which has the same proportionate composition as in the first reaction, provided the temperature be the same. Thus it makes no difference from which end the start is made, a condition of equilibrium results in which *the amounts, or* **concentrations,** *of the components* are the same.

These relations have been proved to be so constant that they have found mathematical expression. *The product of the concentrations of all the factors on one side of an equation is equal to the product of the concentrations of all the factors on the other* side of the equation multi-

plied by a constant quantity. This may be expressed algebraically as follows

$$A \times B \times C \times D \text{ ect.} = X \times Y \times Z \text{ ect.} \ldots \times K$$

or

$$\frac{A \times B \times C \text{ ect.}}{X \times Y \times Z \text{ ect.}} = K$$

where A, B, C, X, Y, Z ect., refer to the concentrations of the different substances,* molecules, atoms or ions as the case may be, which enter into the reaction, and K is a constant quantity depending on conditions for its value but, once determined, remaining unchanged for these conditions. This equation is known as the **equilibrium equation.**

Let the condition of equilibrium in the reaction already considered be expressed by the equation

$$A \times B = X \times Y \times K$$

in which A represents the concentration of alcohol, B of acetic acid, X of ethyl acetate and Y of water. If one of these factors, as A, be increased, the product AB will be larger than the product XYK and the algebraic expression will not be true without a readjustment of values on both sides.

Just as the algebraic equation is rendered untrue by the increase in one of its factors, so is the chemical **equilibrium disturbed** by the increase in the concentration of one of its components. A reaction will take place by virtue of which the concentration of the factors A and B will be lessened while the concentration of X and Y will be increased until equilibrium ensues, when the equation will be true again.

These **relations hold in practice.** If it is desirable to convert one gram of acetic acid entirely into ethyl acetate, it has been found advantageous to increase decidedly the amount of alcohol present beyond that which is sufficient to unite with the acid. Because of the mass of the alcohol present it causes the reaction to run in the direction which will tend to reduce its concentration, *i. e.,* to use it up by forming ethyl acetate. Thus is equilibrium between the components brought about.

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* The equilibrium equation must contain a factor representing each unit (molecule, atom or ion) which enters into the reaction whether they be the same or different. Hence if two molecules (atoms or ions) of the same substance appear in the equation, the factor representing the concentration of this substance must be repeated as $A \times A$, *i. e.,* A^2. If three molecules (atoms or ions) of the same substance enter the reaction, the factor becomes A^3.

Such action of a reagent in shifting the condition of equilibrium because of the large excess in which it is present is known as **mass action.** By increasing the concentration of the components on one side of an equation, or conversely, by decreasing the concentration of the components on the opposite side, mass action may be brought about.

Considering the same reaction after equilibrium has been reached, if the concentration of water present be decreased, the equilibrium will be disturbed and the alcohol and acid will combine. This will lessen the concentrations on the side of the larger product and increase the concentrations on the smaller side, thus restoring equilibrium.

To consider another very instructive illustration: The process of dissociation is a typical reversible reaction which always comes to a condition of equilibrium between the ionized and un-ionized portions of the substance in solution. The **degree of dissociation,** *i. e.,* the ratio between the ionized and non-ionized portions, depends largely upon the dilution of the solution. This is a direct consequence of the mass action relation, as can be demonstrated readily.

Let common salt be put into aqueous solution to an amount sufficient to make the concentration of the dissolved substance equal to unity. *Concentrations are expressed in molecules, atoms or ions of the active agents in a reaction* as the case may be. *Whenever the same number of molecules, atoms or ions are present* in a given volume, *the concentrations are equal.* Suppose the dilution to be such that the salt is one-half dissociated. The number of undissociated molecules is one-half the total number of molecules added; the concentration of undissociated salt is, therefore, $\frac{1}{2}$. The number of molecules of the dissociated salt is equal to the number of molecules undissociated. But each molecule of NaCl that dissociates separates one $\overset{+}{\text{Na}}$ and one $\overset{-}{\text{Cl}}$ ion. Therefore, the number of $\overset{+}{\text{Na}}$ ions is equal to the number of undissociated molecules; the concentration of $\overset{+}{\text{Na}}$ ions is, therefore, $\frac{1}{2}$. Chlorin ions are present to the same concentration also. The general equation for the dissociation of a binary electrolyte, *i. e.,* one which forms two ions only, is

$$A = X \times Y \times K$$

It becomes in this instance

$$\tfrac{1}{2} = \tfrac{1}{2} \times \tfrac{1}{2} \times K$$

in which case $K = 2$.

Suppose, now, that the solution be diluted to twice its volume. The number of molecules of undissociated salt in unit volume of solution is now one-half of its former value. Its concentration will be one-half the former concentration, or $\frac{1}{4}$. Similarly the concentrations of $\overset{+}{\text{Na}}$ and $\overset{-}{\text{Cl}}$

ions will be halved. Since the constant quantity K is not influenced by dilution of the solution, it will be unchanged. The equation becomes then:

$$\frac{1}{4}=\frac{1}{4}\times\frac{1}{4}\times 2$$

which is untrue. The product of the factors on the right side is much smaller than the concentration of the left side. Ionization takes place, reducing the concentration of undissociated salt and increasing the concentrations of the ions until the equation is once more true. Thus dissociation is directly dependent on the dilution of the solution.

When the volume of the solution is so large that further dilution gives no evidence of further dissociation, the substance is said to be in a state of **complete dissociation.** According to these relations, however, there must still be present a minute amount of undissociated salt, the concentration of which is practically zero.

The conceptions of equilibrium and mass action lie at the foundation of any understanding of chemical reactions. Operating according to the relations just explained, certain physical properties of components in the reactions often act as **determining factors** and cause the condition of equilibrium to be such that the concentration of certain factors becomes practically, if not actually, zero. Because of this relation we can predict that *whenever a gaseous, insoluble or slightly dissociating substance can be formed, it will be formed so long as there are factors present capable of forming it.* This statement applies chiefly to reactions taking place in solution but the formation of a volatile product is a determining factor in reactions performed in the "dry way" as well.

Let us consider the substances AX and BY in solutions so dilute as to be completely dissociated into the kathions $\overset{+}{A}$ and $\overset{+}{B}$ and the anions $\overset{-}{X}$ and $\overset{-}{Y}$. On partial evaporation of the mixed solutions, in the absence of any determining factors, the kathion $\overset{+}{A}$ would unite with the anions $\overset{-}{X}$ and $\overset{-}{Y}$ in proportions determined by the concentrations of the various ions present. In a similar way $\overset{+}{B}$ will unite with $\overset{-}{X}$ and $\overset{-}{Y}$, giving a mixture of AX, AY, BX and BY. A condition of equilibrium will result in which these four substances may be considered as ionizing and reacting together in all possible ways, but to such a degree that the proportions between the constituents are not changed.

If, however, one of the substances, as AY, be gaseous, it will, as soon as formed, pass out of the solution and be incapable of affecting the reaction in any way. By the fact that AY is volatile its concentration is kept continually reduced to practical zero. The ions $\overset{+}{A}$ and $\overset{-}{Y}$ keep coming together to form more undissociated salt in the endeavor to bring about an equilibrium which is continually disturbed by the volatility of AY. If the reaction speed is sufficiently great, all of AY will be formed in a very short interval of time and will pass out of solution. There will be left in solution nothing but $\overset{+}{B}$ and $\overset{-}{X}$ to form undissociated BX on evaporation of the solution. Thus a **gaseous product** determines the direction in which a reaction will go by keeping the concentration of the constituents forming it reduced to zero.

An **insoluble substance** acts in exactly the same way. If the reaction be one that takes place in solution only, an insoluble substance suspended in the liquid, however finely divided, will no more be present in solution or affect the reaction than a glass rod in the beaker. The difference between the insoluble substance inside the beaker and surrounded by solution and the gaseous substance unquestionably removed from the sphere of action is apparent and not real.

If AY be a non-volatile soluble **substance dissociating but little** in comparison with AX, BX and BY, it determines the reaction none the less definitely. Most reactions in solution take place between ions only. If AY does not dissociate appreciably, the concentrations of ions $\overset{+}{A}$ and $\overset{-}{Y}$ is kept less than is necessary for equilibrium and they are removed from the sphere of action just as completely as if AY were gaseous or insoluble.

Certain of these determining factors may exercise an influence under one condition in which a reaction takes place and not under other conditions. Hence the products of a reaction may be very different under one condition than under another, although the matter present may be the same. This point is illustrated on a world scale by the fact that the characteristic compounds of igneous rocks are anhydrous silicates while hydrated silicates and carbonates are typical of all later formations. This difference is due to the fact that at high temperatures water and carbon dioxid are both volatile and were thus removed from the sphere of action. Under the conditions maintaining on the earth to-day water is an ever-present factor. Carbon dioxid is quite soluble in it and therefore the process of hydration and decomposition of the silicates known as "weathering" is accompanied by the formation of carbonate deposits. **With the temperature the equilibrium shifts.** That which under former conditions was the stable phase is to-day unstable.

In a similar way, from boric acid and sodium carbonate in solution sodium tetraborate, $Na_2B_4O_7.10H_2O$, crystallizes, while at the fusion temperature sodium metaborate, $NaBO_2$, is formed.

In the present consideration it has been assumed that the solutions of the reagents AX and BY are so dilute that the dissociation is complete. This is by no means essential to the proposition. In **concentrated solutions** a small fraction only exists in the ionized condition; the proposition is true, nevertheless. As the concentration of the ions $\overset{+}{A}$ and $\overset{-}{Y}$ are reduced to zero by the volatility, insolubility or non-dissociation of AY, the equilibrium between the dissociated and undissociated portions of AX and BY is disturbed in each case. This leads to further dissociation of each salt until finally all of AX and BY have been ionized and reacted. By the operation of the same principles in the reverse direction the ions $\overset{+}{B}$ and $\overset{-}{X}$ which are left in solution may become undissociated BX to a large degree.

The actual number of ions present in solution at any one time may be but a small fraction of the total number of ions that might exist at a greater dilution. It is not the actual number of ions present that determines the extent to which a reaction will take place or the amount of product that will be formed, but rather the total number of ions of a given kind that it is possible to form during the course of the reaction. Ions not actually existent at any one time but possible of formation during the course of a reaction are known as **potential ions.**

In practical work it is not sufficient ordinarily to rely on reactions in which part only of the reagents interact while an appreciable fraction is unchanged. Reactions of this kind, moreover, do not generally give definite visible evidence that a reaction is taking place. For use in analytical chemistry such reactions are chosen as contain within themselves some determining factor to cause the practical completion of the reaction and at the same time give visible evidence that a change has taken place. Hence, such reactions as are accompanied by the formation of a **precipitate,** the evolution of a **gas** or a **change in color** are primarily important in formulating a scheme of analysis.

HYDROLYSIS.

To learn something of the application of the principles of equilibrium and mass action to the phenomena of dissociation, let us consider the ionization of what may be termed **unbalanced salts.** By this term is meant normal salts formed by the action of strong bases on weak acids or the reverse. Such salts are to be distinguished from the *balanced* normal salts formed by the neutralization of acids and bases which dissociate to approximately the same degree. Unbalanced salts do not contain within themselves hydrogen or oxygen capable of forming either hydrogen or hydroxyl ions and they are, therefore, entirely different from basic or acid salts. Sodium carbonate is such an unbalanced salt, being formed by the action of the strong base, sodium hydroxid, on the weak carbonic acid.

Let it be remembered that a strong base or acid dissociates with great readiness while a weak base or acid dissociates but little. Salts ionize readily, however. Sodium carbonate, Na_2CO_3, may be taken as a type of all other **salts of strong bases with weak acids.** When it goes into solution, it ionizes to a great extent, giving at once a high concentration of sodium and carbonate ions.

The neutralization of dilute acid with dilute solutions of the strong bases has been set forth as consisting essentially of the union of hydroxyl ions with hydrogen ions to form **water.** The formation of water from its ions of course implies dissociation into these ions. This is a fact and water may be considered either as a very weak acid or base. *Water* is to be remembered, however, as a substance which *dissociates to an extremely small degree,* only about one or two in a thousand million molecules being ionized. Compared with compounds which dissociate readily this becomes relatively zero and may be entirely disregarded. In dealing with substances which dissociate but little, these values often become significant. It is so in the present consideration.

Sodium carbonate introduces into solution a high concentration of $\overset{=}{CO}_3$ ions and of $\overset{+}{Na}$ ions. Water supplies a relatively small concentration of $\overset{-}{OH}$ and $\overset{+}{H}$ ions. With these four ions as factors, there is the possibility of the formation of NaOH and H_2CO_3. Sodium hydroxid ionizes readily; therefore the undissociated substance will not be formed, but the ions will stay in solution in undiminished concentration. Carbonic acid, on the other hand, dissociates to an exceedingly small degree. The product of the large factor — the concentration of $\overset{=}{CO}_3$ ions — by the small factor — the concentration of $\overset{+}{H}$ ions — is too great for the equilibrium between the dissociated and undissociated H_2CO_3. A reaction takes place to decrease the concentrations of the ions and to increase the concentration of the undissociated substance. The ions come together to form undissociated carbonic acid.

By this removal of hydrogen ions from the sphere of action, the equilibrium between the dissociated and undissociated water is disturbed and more water dissociates. Thus the concentration of $\overset{+}{H}$ ions is raised to quite the original figure. This fact again causes the formation of more undissociated H_2CO_3. The dissociation of water and the formation of undissociated acid from its ions continues until equilibrium is reached. There will remain an excess of $\overset{-}{\mathrm{OH}}$ ions which gives the solution the characteristic basic reaction to litmus and other dyes.

When a salt is thus broken down by means of water into the corresponding acid and base, the process is called **hydrolysis.** Hydrolysis is a general phenomenon taking place whenever a salt of a weak acid or base goes into solution. Under ordinary conditions, because of the exceedingly small amount of dissociated water present, the proportion of salt actually hydrolyzed is very small, ordinarily not over one per cent. This proportion is sufficient to be readily indicated by litmus paper, however. In some cases the presence of the free acid may be indicated by the odor, although the solution gives the basic reaction. Solutions of the alkali salts of the volatile hydrocyanic, hydrosulfuric and sulfurous acids exhibit these phenomena to a considerable degree.

If solutions of the **salts of weak bases with strong acids** be investigated, exactly the reversed phenomena will be observed. Ferric chlorid is such a salt, ferric hydroxid being a very weak base while hydrochloric acid dissociates readily. On going into solution ferric chlorid gives high concentrations of $\overset{+++}{\mathrm{Fe}}$ and $\overset{-}{\mathrm{Cl}}$ ions. The dissociated water gives low concentrations of $\overset{-}{\mathrm{OH}}$ and $\overset{+}{\mathrm{H}}$ ions. The product of the large factor — the concentration of ferric ions — by the small factor — the concentration of $\overset{-}{\mathrm{OH}}$ ions — is too great for the equilibrium between dissociated and undissociated ferric hydroxid. The equilibrium reaction takes place, reducing the concentration of the dissociated salt by the formation of the undissociated base, $\mathrm{Fe(OH)_3}$. An excess of $\overset{+}{\mathrm{H}}$ ions remains that gives to the solution an acid reaction.

The fact that ferric hydroxid is insoluble aids this reaction very materially. Ferric hydroxid accumulates as a precipitate, therefore, until the concentration of acid becomes sufficient to dissolve it and form ferric chlorid and water once more. Thus the system comes to equilibrium. It is maintained in this condition by the continuous formation of free acid and base by hydrolysis, and the formation of the salt by the neutralization of the one by the other. It is, however, only necessary to remove the acid by appropriate means in order that complete hydrolysis may take place and all the ferric hydroxid be precipitated.

If there be a considerable difference between the strengths of the acid and the basic constituent of a salt, hydrolysis will give to its aqueous solution the reaction of the constituent which dissociates to the greater extent.

REPRESSION OF IONIZATION.

In dilute solutions the dissociation of a substance is not ordinarily affected appreciably by other substances present in reasonably small amounts, provided they do not combine directly with any of the ions present. If, however, two substances are capable of forming a **common ion,** they will have a decided effect on each other especially if one dissociates more readily than the other. Acetic acid and its salts illustrate this phenomenon very satisfactorily and furnish an instance of great interest to analytical chemistry.

In dilute **acetic acid solutions** only small concentrations of hydrogen and acetate ions are present, since at the ordinary dilution, the ionization of acetic acid is only four per cent. of that given by hydrochloric acid. For this reason many reactions will take place in acetic acid solutions which cannot be brought about in solutions of the mineral acids. In the equation representing the equilibrium between the dissociated and undissociated acid, the factors representing the concentrations of the hydrogen and acetate ions are equal.

If a considerable amount of **sodium acetate** or other salt of acetic acid be added to the solution, since salts dissociate readily, a high concentration of metallic ions and of acetate ions is introduced. The total concentration of acetate ions is now many times the concentration produced when the acetic acid first came to equilibrium with its ions. Consequently, the initial equilibrium is disturbed and a reaction ensues to lessen the concentration of the ionized portion of the acid. Hydrogen and acetate ions come together, an equal number of each, to form undissociated acid. But since the concentration of acetate ions was increased by a very considerable factor, the concentration of hydrogen ions must be decreased correspondingly until equilibrium is reached.

In the equation representing this final condition of equilibrium the concentration of acetate ions is a very large factor while the concentration of hydrogen ions is very small. In this way the concentration of hydrogen ions, consequently the acidity of the solution, is greatly reduced without neutralization or removal of the acid. This phenomenon is known as the **repression of ionization.** *Whenever a strongly dissociating electrolyte is added to a solution of a slightly dissociating substance, the ionization of the weaker one is thereby repressed, provided the two substances have a common ion.*

As a further illustration of this same principle the action of salts of ammonium upon the free base may be cited. **Ammonium hydroxid** is a weak base, at ordinary dilutions dissociating only to about one-fourhundredth of the extent to which sodium and potassium hydroxids ionize. By the addition of the chlorid or other salt of ammonium to its solutions the concentration of hydroxyl ions may be much further reduced. **Ammonium chlorid** dissociates readily, introducing a high concentration of ammonium ions which disturbs the original equilibrium between the undissociated base and its ions. Ammonium ions unite with hydroxyl ions, therefore, to increase the concentration of the undissociated base and decrease the concentration of the ions. By the removal of hydroxyl ions from the solution its basic properties are lessened. This principle finds frequent application in the separation of the different metals in qualitative analysis. (See pages 265 and 269.)

X Friday

SOLUTE AND SOLVENT.

When a substance, technically known as the **solute,** is brought in contact with a **solvent,** it dissolves, the proportion of solute to solvent increases from zero* until a certain definite ratio between the solute and the solvent is reached which is known as the **solubility** of the substance dissolved. *The solubility of a substance expresses the proportionate composition of a solution which is at equilibrium with the solute in contact with it;* that point at which as much goes into solution as separates from it in any given interval of time. A solution which is at equilibrium with the solute is said to be a **saturated solution.**

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Most solids dissolve to a greater degree in hot solvents than in cold solvents and the solubility is said to increase with the **temperature.** Liquid solutes are affected much less regularly by temperature, while the solubility of gaseous solutes decreases as the temperature increases.

If a solution of a solid prepared at a high temperature be cooled, as its solubility decreases with the temperature, it will contain more of the solute than it can hold and still be in equilibrium. A solution in this condition is said to be a **supersaturated solution.**

The normal tendency of such a supersaturated solution is to separate the excess from solution. This readily occurs if some of the solid be in contact with the solution. If no solid solute be present, however, solutions of some substances show a surprising tendency to remain in a highly supersaturated condition for some time, especially if the solution be not disturbed. Separation of the excess can usually be induced by vigorous shaking or by adding a minute particle of the solid substance.

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* As the amount of solvent contained in a given amount of solute increases from zero the specific gravity of the solution changes slowly and may become either greater or less than the specific gravity of the pure solvent. At any given temperature there is a definite specific gravity for each definite proportion between solute and solvent. Many common substances have been carefully investigated in this respect. Hence it is possible to ascertain the concentration of a solution of these substances simply by determining the specific gravity. (See pages 322 and 323.)

If the separation takes place comparatively slowly, *large regular-shaped forms* result, *the physical properties of which usually vary with the direction through the mass.* Such forms *are known as* **crystals** and the process of separation of the solid from the solvent as *crystallization.*

Many substances in separating from solution in crystal form take up a definite amount of the solvent which is an essential constituent of the crystal to which many of its properties, especially its color, are due. While this phenomenon is not confined to any particular solvent, water shows especial tendencies in this direction and when so incorporated in the crystalline structure is known as **water of crystallization.**

Water of crystallization shows none of the ordinary properties and is undoubtedly combined in some way with the solid substance. The combination is less stable than many of the known chemical compounds, for the water is usually driven off when the temperature is raised much above 100° and then shows all its characteristic properties.

Under ordinary conditions certain crystals tend to lose their water of crystallization, giving it up to the atmosphere surrounding them. Such substances are said to be **efflorescent.** On the other hand certain substances are able to take up moisture from the atmosphere and are said to be **hygroscopic.** The absorption and condensation of water from the atmosphere continues in some cases until the substance passes into solution, this phenomenon being known as **deliquescence.** It is to be noted, however, that these phenomena depend essentially upon the amount of water vapor present in the atmosphere and the same substance that is efflorescent in a dry region may be deliquescent in the presence of moisture.

A substance which is free from water is said to be *anhydrous.*

If the separation of the solute from the solvent takes place rapidly, the product is finely divided and is called a precipitate, the process being known as precipitation.

The **precipitate** may be *crystalline, micro-crystalline* or *pulverulent* (like powder), depending on the size of the crystals formed or, if the particles are so small as to be apparently without definite shape, the precipitate may be *flocculent, clotted* or *gelatinous.* In every case, however, *the solution from which a precipitate separates is* still saturated *with the precipitated substance.*

If it be desired to separate a substance as completely as possible from solution, conditions must be brought about under which the solubility of the substance is small; otherwise much of the solute will be still contained in the saturated solution. If, for instance, it is desirable to separate barium as completely as possible from solution, it is necessary to decide in what form to precipitate it. One must take into consideration the facts that in a saturated solution of barium hydroxid there is 1 part of the solute to 20 of water, of barium carbonate, 1 part to 50,000 of water, and of barium sulphate, 1 to 400,000. Hence it is not wise to attempt to precipitate as the hydroxid, because that would leave behind one part of hydroxid in every 20 parts of water, but rather as sulfate, which will leave only one part of the salt in 400,000 of water.

Substances which have extremely small solubilities are often said to be **insoluble** in distinction from those which have fairly large solubilities which are known as **soluble.** There are no substances which are truly insoluble, although from the standpoint of qualitative analysis many are practically insoluble.

The term precipitation is restricted usually to substances which are fairly insoluble, while the word crystallization applies to those which are readily soluble.

Water is always understood to be the solvent to which reference is made when no other solvent is specially mentioned.

Qualitative analysis consists largely of a study of **comparative solubilities.** To a solution which may contain many different substances, a reagent is added often capable of reacting with each. Some of the reaction products are so slightly soluble that the first trace formed will be sufficient to saturate the liquid and the remainder will then separate as an insoluble precipitate. Other reaction products will have such large solubilities that the total amount formed will not be sufficient to saturate the solvent present, hence all will remain in solution. Because of such differences in solubility, separations are readily effected.

Since the method of classifying the elements into groups according to any scheme of qualitative analysis depends alone on the varying solubilities of the compounds formed, it does not necessarily mean that those elements that most closely resemble each other in their chemical properties and their compounds will be found in the same group. The metals mercury, cadmium, zinc and magnesium closely resemble each other, yet are found two of them in Group I, one in Group III and one in Group V, owing chiefly to very varying solubilities of their respective sulfids. The **grouping of elements in qualitative analysis** denotes similar solubilities of similar salts of the different metals in any group and nothing further.

The most satisfactory classification of the elements into groups based on chemical similarity in properties is known as the Periodic System and is given on pages 64 and 65.

An interesting case of the interworking of the laws governing solution and ionization may be developed from a consideration of the phenomena resulting when substances insoluble in water are treated with solutions of acids. *The* **insoluble salts of weak acids** *dissolve in solutions of strong acids, but the insoluble salts of strong acids will not dissolve in the solutions of other strong acids.*

When **calcium phosphate** comes in contact with water, it forms a saturated solution. Practically all of the dissolved salt exists in the ionic condition, for the dilution is large since the solubility is small. There is equilibrium between the ions and the undissociated salt and between the dissolved and the undissolved portions as well. If any strong acid be added, it introduces a relatively high concentration of hydrogen ions. This factor taken into consideration with the concentration of phosphate ions introduced by the dissolved salt is too great for equilibrium between dissociated and undissociated phosphoric acid since this acid dissociates to a small degree only. By the equilibrium reaction undissociated phosphoric acid is formed, the concentration of phosphate ions is lessened and the equilibrium between the dissolved and undissolved portion of the salt is disturbed. More salt passes into solution to restore the original concentration of phosphate ions. This causes the formation of more undissociated phosphoric acid and a second adjustment of concentrations becomes necessary. In this way the slightly soluble salt dissolves readily as long as there is a high concentration of hydrogen ions in the solution.

There remains in solution an abundance of calcium kathions and the anions of the acid added. The phosphoric acid is for the most part undissociated. By the application of the principles of equilibrium and mass action alone it is thus possible to explain how the "stronger acid takes the base from the weaker acid."

Insoluble hydroxids are all readily soluble in acids and are to be considered as salts of the very weak acid, HOH. Many, probably all, **oxids** unite with water to form hydroxids to some extent at least. Their solubility in dilute acid solutions is to be explained exactly as the solubility of the hydroxids.

On the other hand, solution of the very-slightly-soluble silver chlorid is not appreciably aided by the addition of the strong nitric acid, although both of the products of the possible metathesis, silver nitrate and hydrochloric acid, are extremely soluble. The conditions of equilibrium between the ionized and non-ionized portions, and the dissolved and undissolved portions of the silver chlorid are not disturbed by the highest concentrations of hydrogen ions obtainable. There is no tendency toward reduction in the concentration of any of the ions present in solution by the formation of undissociated substances since all the compounds possible of formation dissociate to a very high degree. Hence the system maintains the equilibrium which it first reached.

The hydroxids of lead, tin, zinc and aluminum, substances insoluble in water, furnish another application of the same principle by their **solubility in strong bases.** Here water plays the part of a weak acid (see pages 29 and 176). In the presence of a high concentration of hydroxyl ions from sodium or potassium hydroxid (ammonium hydroxid is not sufficiently dissociated), lead hydroxid, PbO_2H_2, acts as an acid and separates hydrogen ions (see pages 22 and 143). Water is formed from these components and the initial equilibrium disturbed. The lead hydroxid continues to dissolve and water continues to form until all the lead hydroxid has passed into solution. There is left an abundance of the ions $P\overline{b}O_2$ and $\overset{+}{N}a$ to form the salt, sodium plumbite, Na_2PbO_2.

In general, *whenever any reagent is added to a saturated solution of an insoluble substance, the solution being in contact with an excess of the solute, if the added reagent causes the concentration of the ions of the solute to become less, the insoluble substance tends to dissolve.*

SEPARATION OF SOLIDS FROM LIQUIDS.

A liquid may be separated from a substance dissolved in it by causing the liquid to become volatile or to pass into the gaseous state. Such a method of separation is not applicable when both solute and solvent are volatile under the same conditions. If the liquid is not retained, the process is known as **evaporation.** At high temperatures evaporation takes place more rapidly than at low temperatures. At ordinary temperatures it is said to be spontaneous.

If, in the separation of solute from solvent, the liquid be collected, the process is called **distillation.** The liquid is usually caused to evaporate rapidly by applying heat. The vapors are liquefied again by passing through a cooling apparatus called a condenser. The condensed liquid, thus separated from all non-volatile substances, is known as the **distillate.**

A liquid may be separated from substances suspended in it by straining it through a porous membrane, the size of the pores being such that while the particles of the liquid are readily allowed to pass through, the passage of the suspended matter is prohibited. This membrane is known as the **filter**; the liquid passing through its pores is called the **filtrate** and the suspended matter retained by the filter is termed the **residue** or **precipitate.**

The process of **filtration** is merely a mechanical screening out of the suspended matter because the size of these particles is very much larger than the molecules of the liquid. Obviously the size of the particles to be removed will determine how small the diameter of the pores in the filter must be to effect a separation. Almost any powder which can be obtained mechanically may be satisfactorily separated by ordinary filter paper.

Just as the particles of a solid substance move over each other with friction, so do the molecules of a liquid move with friction on each other. Friction between molecules as distinguished from friction between masses is called internal friction, or, more often in the case of liquids, **viscosity.** Since heat increases the freedom of motion of the molecules of a body, the viscosity of a liquid is lessened. For this reason it will pass through a filter much more rapidly when hot than when cold. It is expedient, therefore, to filter all liquids as hot as they can be conveniently handled unless there is some definite reason for doing otherwise.

By certain chemical reactions it is possible to produce precipitates so finely divided that they will pass through the finest filter. The particles are so minute as to be invisible to the most powerful microscope. The liquid in which they are suspended, appears perfectly clear and has all the appearance of a solution, although its properties are those of the pure solvent. Such a finely divided precipitate is known as a **colloidal precipitate** or as a **pseudo-solution.**

On boiling a pseudo-solution the particles generally coalesce, the liquid becomes turbid and may then be filtered in the ordinary way. By the addition of a strongly dissociating substance to the pseudo-solution a visible precipitation may often be effected.

Other precipitates are frequently met, intermediate in size between the colloidal precipitate and that which may be readily filtered. Sometimes these may be so finely divided as to run through the filter paper. This may often be prevented by using two filters instead of one or by pouring the **cloudy filtrate** back onto the paper repeatedly. The pores in the filter will gradually become filled with the precipitate to such an extent that the filtrate will finally run through clear. By allowing a finely divided precipitate to stand for some time in hot water, the particles often coalesce and become more crystalline after which they may be readily filtered.

Sometimes a precipitate, on standing in contact with a cold solution, will exhibit a tendency toward the formation of colloidal precipitates. The result is the formation of a **slime** which clogs the filter and makes the process of filtration exceedingly slow and tedious. As the tendency toward the formation of colloidal solutions decreases as the temperature rises, rapid filtration is assured by the use of hot liquids.

The regulation round filter should be folded twice to form a quadrant and then opened so as to form a cone with three thicknesses of paper on one side and one on the other. In this shape it should be inserted in the funnel and the paper fitted to the glass by adjusting the folds a trifle if necessary. Moisten with water and press firmly against the sides of the funnel so that the filter and funnel are everywhere in contact. When a solution is poured upon a properly **fitted filter,** the stem of the funnel will fill with the hot filtrate, the weight of which will tend to suck the liquid through the paper and make the process more rapid than if the filter is laid loosely in the funnel.

In order to separate the precipitate completely from the filtrate, it should be allowed to drain as dry as possible, after which it is necessary to wash it. Hot water should ordinarily be used, since a small volume will dissolve any adhering substances to a greater degree than the same volume of cold water. For the reasons already considered, washing with hot water tends to keep the precipitate in better condition than cold water. After each **washing, the precipitate** should be allowed to drain thoroughly before more water is poured onto the paper.

If the precipitate settles rapidly and it is undesirable for any reason to separate it by filtration, the liquid may be poured off as completely as possible and hot water added and the mixture shaken. After allowing the precipitate to settle again the wash water may be poured off and the precipitate treated as before. This process is known as **washing by decantation.**

OXIDATION AND REDUCTION.

When heated in air or an atmosphere of oxygen, many substances gain in weight. Because of the chemical activity of oxygen at high temperatures, they unite with it and form oxids. This process is known as **oxidation.**

On the other hand, when oxids are heated in an atmosphere of hydrogen, they lose their oxygen since it unites with hydrogen to form water. This process is called **reduction** and is the reverse of oxidation.

Certain non-metallic elements, other than oxygen but equally reactive, behave in a very analogous manner under the same conditions. Hence it is customary to extend these conceptions and to consider as *oxidation any process in which a non-metallic element is added to a substance or hydrogen is removed from it. Reduction is any process in which a non-metallic element is taken away from a substance or hydrogen is added to it.*

That the **removal of hydrogen is equivalent to the addition of oxygen,** and vice versa, can best be shown by a concrete illustration. If ammonia, NH_3, be oxidized, we may consider that the oxygen attaches itself directly forming a compound, NH_3O. If this new compound subsequently decomposes into NH and H_2O, it does not lessen the fact that NH is an oxidation product of NH_3 as well as H_2O. Yet NH is simply NH_3 from which hydrogen has been removed. Further oxidation may remove all the hydrogen and later add oxygen. In the oxidation of ammonia all of the following steps are conceivable and all are known with the exception of the third:

$$2NH_3 \quad N_2H_4 \quad N_2H_2 \quad N_2 \quad N_2O \quad N_2O_2 \quad N_2O_3 \quad N_2O_4 \quad N_2O_5$$

Looked at from the other direction, each one of these bodies may be regarded as a reduction product of N_2O_5, in which case reduction is seen to be no less a removal of oxygen than the addition of hydrogen. N_2O_5 is to be regarded as the highest oxidized product of ammonia and NH_3 as the lowest reduction product of nitrogen pentoxid.

Any substance which causes oxidation is called an **oxidizing agent.** Any substance causing reduction is known as a **reducing agent.**

Oxidation and reduction are reciprocal terms. One process can not take place without the other. If one substance gives up its non-metallic constituents wholly or in part to another substance, the latter is oxidized, but the oxidizing agent is itself reduced. Hence *any substance which is readily oxidized is a reducing agent and any substance which is readily reduced is an oxidizing agent.*

Under these circumstances it is not surprising to find that certain substances may be **either oxidizing or reducing agents** depending on the conditions present. In the presence of a strong oxidizing agent they may act as reducing agents, while in the presence of a strong reducing agent they may act as oxidizing agents.

Those elements which are ordinarily used as oxidizing agents are oxygen, chlorin, bromin and iodin, together with compounds from which these elements may be readily liberated.

Hydrogen, carbon and compounds containing these elements in considerable proportions are the ordinary reducing agents. Sulfur and its compounds are used as reducing agents also, but the element and its dioxid may act as oxidizing agents in the presence of stronger reducing agents.

By far the most active reducing agent known is hydrogen, especially at the moment when it is liberated from a compound. If a metal be thrown into a solution of an acid, any substance present in solution with the acid will be reduced more quickly than if the hydrogen is collected and then bubbled through a similar solution. When in this very active state, it is said to be in the **nascent condition.**

Possibly the most satisfactory **explanation** that has been offered of this phenomenon is concerned with the structure of the molecule. The molecule of gaseous hydrogen is known to consist of at least two atoms joined to each other. This structure may be represented graphically by the formula $\mathrm{H}-\mathrm{H}$, each atom being linked to its fellow by a single bond since hydrogen is a univalent element. For an instant after its liberation from a compound it is thought to exist in the atomic condition, the atoms being not yet joined together. This condition may be represented by the symbol $\mathrm{H}-$, the free bond indicating that the atom exists alone uncombined with any other. It is easily conceivable that any substance would be more active when its atoms were free than when joined together in pairs or otherwise to form molecules, since in the latter condition the molecule must be broken up before its atoms can unite with the atoms of other substances.

Elements other than hydrogen exhibit similar phenomena. The nascent condition of an element may be indicated by **free bonds** attached to the symbol for its atom, one bond being added for each valence shown. Nascent chlorin, being univalent, is represented by the symbol $\mathrm{Cl}-$ nascent oxygen, being divalent, is represented by the symbol $\mathrm{O}=$.

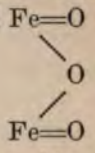
Hydrogen is the **best reducing substance** known, yet a compound in which hydrogen is present to only a small proportion may be a more active reducing agent than hydrogen gas, provided it can be made to liberate its hydrogen in the nascent condition. Similarly oxygen gas is not necessarily the **best oxidizing agent,** for any substance which will liberate nascent oxygen will be a more active oxidizing agent. Hence it is that many compounds are known which are more active oxidizing agents than air or even pure oxygen.

In the reactions with which qualitative analysis is concerned, the following substances act as **oxidizing agents**:

(*a*) Oxygen
Sulfur
Chlorin
Bromin
Iodin

(*b*) Nitrous acid, HNO_2
Nitric acid, HNO_3
Hypochlorous acid, $HClO$
Chloric acid, $HClO_3$
Permanganic acid, $HMnO_4$
Chromic acid, H_2CrO_4*
Dichromic acid, $H_2Cr_2O_7$
Hydrogen peroxid, H_2O_2

(*c*) Stannic salts—from the oxid SnO_2
Ferric salts—from the oxid



Mercuric salts—from the oxid HgO

(*a*) The **elementary substances** usually show their oxidizing action by **direct addition** to the reducing substances, as the following reactions indicate:

(1) $SO_2 + O$† $\rightarrow \mathbf{SO_3}$
(2) $\mathbf{SnS} + \mathbf{S} \rightarrow \mathbf{SnS_2}$
(3) $FeCl_2 + Cl \rightarrow FeCl_3$
(4) $SnCl_2 + Br_2 \rightarrow SnCl_2Br_2$ or, doubling the quantities,
$2SnCl_2 + 2Br_2 \rightarrow SnCl_4 + SnBr_4$.
(5) $2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$

The halogen elements, chlorin, bromin and iodin, frequently act as oxidizing agents when it is preferable to indicate their action as an addition of oxygen rather than of halogen. In such cases it is customary to consider that the **halogens act on water**, decomposing it, forming a hydrogen halogen acid and liberating nascent oxygen which then adds directly to the reducing agent. The following reactions will clearly indicate the nature of the process.

$$2Cl + H_2O \rightarrow 2HCl + O = \qquad HNO_2 + O = \rightarrow HNO_3$$

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* Chromic acid is practically unknown, since it loses water and passes into dichromic acid according to the reaction:

$$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O$$

It is included in the table because its salts are well known.

† Although it is a well-established fact that the molecules of non-metallic elements consist of at least two atoms, no attempt will be made to introduce at least a molecule of all elements into equations when simplicity is to be gained by representing only a single atom.

Both reactions may be combined in one.

$$HNO_2 + 2Cl + H_2O \rightarrow HNO_3 + 2HCl$$

(*b*) All of this group of oxidizing agents are acids. Salts of these acids, especially the sodium and potassium salts, are frequently used instead of the acids. The lead and manganese salts of hydrogen peroxid, lead and manganese dioxids, are quite as commonly used as sodium peroxid. Since a salt is generally more stable than the corresponding acid, as an oxidizing agent **a salt is less energetic than the free acid.**

For the purpose of **simplifying oxidation and reduction** reactions it is often advisable to consider an acid or its salt as composed of an oxid of a metallic element and an oxid of a non-metallic element, hydrogen being considered as a metallic element. Chromic acid, H_2CrO_4, is equivalent to H_2O and CrO_3; potassium chromate to K_2O and CrO_3. None of the oxygen available in a reaction comes from water or the metallic oxid corresponding to it, as K_2O or Na_2O, hence no error is made in disregarding these factors. In this way we may consider

Nitrous acid, $2HNO_2$	as $H_2O + N_2O_3$
Nitric acid, $2HNO_3$,	as $H_2O + N_2O_5$
Hypochlorous acid, $2HClO$,	as $H_2O + Cl_2O$
Chloric acid, $2HClO_3$,	as $H_2O + Cl_2O_5$
Permanganic acid, $2HMnO_4$,	as $H_2O + Mn_2O_7$
Chromic acid, H_2CrO_4,	as $H_2O + CrO_3$
Dichromic acid, $H_2Cr_2O_7$,	as $H_2O + 2CrO_3$
Hydrogen peroxid, H_2O_2,	as $H_2O + O$

Since these non-metallic oxids are acids minus water, they are known as **acid anhydrids.**

That this series of acids and salts act as oxidizing agents is due to the fact that ordinarily in the presence of reducing agents their anhydrids are not as stable as some lower form containing less oxygen. Thus N_2O_2 is the oxid of nitrogen usually formed as a reduction product, hence both nitrous and nitric acids break down into N_2O_2, water and nascent oxygen. The amount of oxygen liberated depends on the difference in the oxygen content between the oxidizing agent and the compound stable in the presence of reducing agents. By the application of this principle an **oxygen equivalent** may be calculated for each oxidizing agent. The conditions of the experiment influence the amount of oxygen liberated somewhat, but the equivalents given by the following equations may be considered as typical.

Nitrous acid (2 mols.), $N_2O_3 \rightarrow N_2O_2 + O=$
Nitric acid[*] (2 mols.), $N_2O_5 \rightarrow N_2O_2 + 3O=$
Chromic acid (2 mols.), $2CrO_3 \rightarrow Cr_2O_3 + 3O=$
Dichromic acid (1 mol.), $2CrO_3 \rightarrow Cr_2O_3 + 3O=$
Permanganic acid (2 mols.), $Mn_2O_7 \rightarrow 2MnO_2 + 3O=$ in neutral or alkaline solution
Permanganic acid (2 mols.), $Mn_2O_7 \rightarrow 2MnO + 5O=$ in acid solution
Hypochlorous acid (2 mols.), $Cl_2O \rightarrow O= + 2Cl$[†]
Chloric acid (2 mols.), $Cl_2O_5 \rightarrow 5O= + 2Cl$[†]
Hydrogen peroxid (1 mol.), $O \rightarrow O=$

By the intervention of a molecule of water in those reactions in which the direct addition of chlorin, bromin or iodin is not to be indicated, the action of the halogen elements may be referred to an oxygen basis and their oxygen equivalent indicated as follows:

$$Cl_2 + H_2O \rightarrow 2HCl + O=$$
$$Br_2 + H_2O \rightarrow 2HBr + O=$$
$$I_2 + H_2O \rightarrow 2HI + O=$$[‡]

[*] One of the commonest oxidizing agents is known as **aqua regia.** It is made by mixing nitric and hydrochloric acids and warming. Since hydrochloric acid is not an oxidizing agent, the oxidizing power of aqua regia must be due entirely to nitric acid. In the proportions of three of hydrochloric acid to one of nitric acid the following reaction takes place:

$$3HCl + HNO_3 \rightarrow 3Cl- \quad + O= \quad + N + 2H_2O$$

Since nascent chlorin attacks many mineral substances far more readily than nascent oxygen, aqua regia is a more general oxidizing agent than nitric acid alone. In this combination nitric acid is broken down to free nitrogen, thus a greater equivalent of oxygen is obtained than is usual with nitric acid.

Aqua regia consists of a mixture of hydrochloric acid, nitric acid, nascent chlorin and nascent oxygen. Its action may be more satisfactorily expressed by these individual reagents, such as are needed, than by attempting to write an equation that should include the whole mixture. The oxidation of mercurous chlorid by aqua regia is best expressed by the equation:

$$\mathbf{(HgCl)_2} + 2Cl- \quad \rightarrow \quad 2HgCl_2$$

The oxidation of nickel sulfid uses other reagents:

$$\mathbf{NiS} + 4O= \quad + 2HCl \rightarrow NiCl_2 + H_2SO_4$$

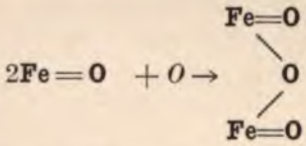
[†] Although hypochlorous and chloric acids decompose in this way, their salts do not. The latter break down into chlorids and nascent oxygen, thus:

$$KClO \rightarrow KCl + O= \quad \text{and} \quad \mathbf{KClO_3 \rightarrow KCl} + 3O=$$

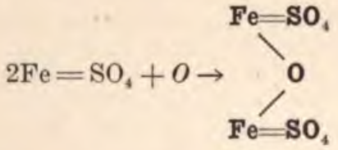
The oxygen equivalents of salt and acid are the same, the only difference being that the salts liberate oxygen only while the acids liberate both oxygen and chlorin.

[‡] This reaction with iodin is not known to take place to an appreciable extent under ordinary conditions, but for the sake of systematization it may be allowed to appear in this connection.

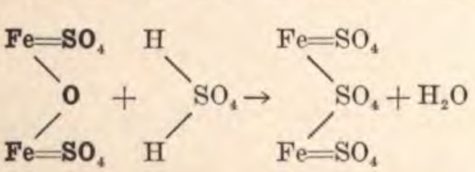
(*c*) Since the salts of any metal may be formed by the action of acids on the various oxids of the metal, these **oxids** offer a simple basis for the consideration of oxidation and reduction reactions. Any bibalent salt of iron may be formed, theoretically at least, by dissolving the bivalent ferrous oxid, FeO, in the necessary acid. Similarly, any trivalent salt of iron may be formed by the action of the necessary acid on the trivalent ferric oxid, Fe_2O_3. The oxidation of ferrous chlorid, $FeCl_2$, ferrous sulfate, $FeSO_4$, or ferrous acetate, $Fe(C_2H_3O_2)_2$ to ferric chlorid, $FeCl_3$, ferric sulfate, $Fe_2(SO_4)_3$, or ferric acetate, $Fe(C_2H_3O_2)_3$, may be considered as the oxidation of ferrous oxid to ferric oxid and the action of the necessary acids on the oxidation product. By this means the oxidation of any particular salt is referred to a general basis and the equations much simplified. For instance, let ferrous sulfate be oxidized by the oxygen of the air. To oxidize ferrous oxid to ferric oxid requires one atom of oxygen for every two molecules of ferrous oxid treated, for



One atom of oxygen will oxidize two molecules of ferrous sulfate in the same way:



This compound may be considered as a mixture of ferric sulfate and ferric oxid in the proportion of $2Fe_2(SO_4)_3$ to $1Fe_2O_3$. Evidently there is need of additional sulfuric acid to convert it entirely into ferric sulfate, for

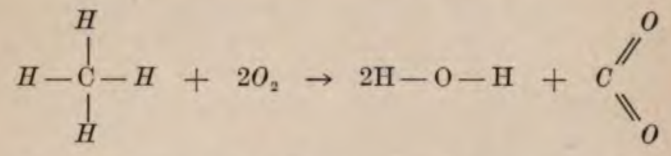


Ferrous sulfate can not be oxidized entirely over into ferric sulfate except in the presence of free sulfuric acid.

From a consideration of this and other similar reactions it is seen that acid is used up in many oxidation reactions. For this reason it is generally true that **oxidation takes place better in acid** than in neutral or alkaline solutions.

From the reactions already considered it will be apparent that the element oxidized generally has its **valence increased.** Divalent iron becomes trivalent, divalent tin becomes tetravalent. Divalent sulfur in hydrogen sulfid, H_2S, oxidizes to the hexavalent condition in sulfuric acid, H_2SO_4. For each atom of oxygen or its equivalent added to an element, its valence is increased by two. Nevertheless increase of valence is not always brought about by oxidation. Hydrogen gas burns to water, marsh gas to water and carbon dioxid. The following equations represent the reactions taking place and show the valences of the elements in each compound:

$$H-H + O \rightarrow H-O-H$$



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H + 2O_2 \rightarrow 2H-O-H + O{=}C{=}O$$

Some elements form a hydroxid corresponding to each of the different valences shown by the element. The valence of **manganese** changes from two to seven and most of the corresponding hydroxids are known. The hydroxid of divalent manganese acts as a fairly strong base and forms salts, such as manganous chlorid, $MnCl_2$, in which manganese plays the part of a metal. The hydroxid of manganese showing seven valences, on the other hand, acts as a strong acid and forms salts, such as potassium permanganate, $KMnO_4$, in which manganese appears in the anion. The hydroxids of manganese showing a valence of three, four and six are intermediate in properties, trivalent manganese acting as a weak base, tetravalent manganese as a very weak acid. Hexavalent manganese forms an acid which is stronger than the corresponding compound of tetravalent manganese, but not so strong as permanganic acid. (See pages 212–220.)

While the hydroxids of **sulfur** are all of an acid nature, sulfurous acid corresponding to the tetravalent condition is much weaker than the hexavalent sulfur in sulfuric acid. Persulfuric acid in which sulfur shows a valence of seven is still stronger. (See pages 184–190.)

Thus it is seen that when an element is oxidized, **with an increase in valence there is a decrease in the basic properties and a corresponding increase in the acid properties of the element** as is shown by the nature of the compounds formed. For this reason the elements forming the *strongest bases are all univalent; divalent bases are less strong. Bases from tri- and tetravalent elements are decidedly weaker.* So weak are they that their salts generally hydrolyze in solution. For these reasons tri- and tetravalent kathions are not so well known as those of a smaller valence. (See pages 11 and 20.) Conversely, a comparison shows that *if an element is capable of forming more than one oxygen* acid, the most highly oxidized compound is the strongest acid.*†

On the other hand, **reduction tends to reduce acid properties and to develop basic properties.** The hydroxid in which chromium shows seven valences is the very strong perchromic acid. Hexavalent chromium forms the strong chromic acid. Trivalent chromium hydroxid acts as a very weak base. (See pages 191–195.)

The very great **difference in the properties of the compounds formed by an element in a highly oxidized condition and the properties of the compounds formed by the same element in a reduced condition** must be constantly borne in mind in making an analysis. After treatment with strong oxidizing agents, manganese and chromium must be sought for among the acids. They will be found among the bases after the introduction of reducing agents. (See pages 263 and 265.)

In many cases **a reducing agent acts more efficiently in an alkaline solution** than in the presence of an acid. For, as oxidation tends to decrease the amount of free acid present by increasing the valence of metallic elements, thus giving them a greater power of combining with acids (see page 44), so, conversely, reduction tends to develop free acid by decreasing the valence of metallic elements, lessening their power of combining with acid radicles and therefore setting acid free.

The common substances which act as **reducing agents** in qualitative analysis are:

Hydrogen
Carbon
Sulfur
Alcohol, H_6C_2O
Oxalic acid, $H_2C_2O_4$
Tartaric acid, $H_6C_4O_6$
Hydrosulfuric acid, H_2S
Sulfurous acid, H_2SO_3
Thiosulfuric acid, $H_2S_2O_3$
Hydrocyanic acid, HCN
Thiocyanic acid, HSCN
Nitrous acid, HNO_2
Hydrochloric acid, HCl
Hydrobromic acid, HBr
Hydriodic acid, HI
Stannous salts — from the oxid $Sn=O$
Ferrous salts — from the oxid $Fe=O$

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* Acids which do not contain oxygen are not included in this generalization.

† The element phosphorus offers an exception to the rule, phosphorous acid, a compound of trivalent phosphorus, being stronger than the pentavalent compound, phosphoric acid.

That these substances act as reducing agents is due to the fact that in the presence of oxidizing agents these compounds are not as stable as some more highly-oxidized forms. Consequently they take up as much oxygen as is necessary to convert them into compounds stable in the presence of oxidizing agents. One substance may not absorb the same amount of oxygen as another. For this reason the values of reducing agents vary considerably. The oxidation products depend somewhat upon the conditions of the experiment, consequently the efficiency of a reducing agent may vary under different conditions. The reactions given below indicate the amount of **oxygen taken up** by each substance under conditions which may be considered typical.

Reducing agent		*Oxygen taken up*		*Compound formed*
Hydrogen (2 atoms), H_2	+	O	→	H_2O
Carbon (1 atom), C	+	O	→	CO
Carbon monoxid (1 mol.), CO	+	O	→	CO_2
Sulfur (1 atom), S	+	2O	→	SO_2
Sulfur dioxid (1 mol.), SO_2	+	O	→	SO_3
Nitrous acid (1 mol.), HNO_2	+	O	→	HNO_3
Hydrocyanic acid (1 mol.), HCN	+	O	→	HCNO
Stannous oxid (1 mol.), SnO	+	O	→	SnO_2
Ferrous oxid (2 mols.), 2FeO	+	O	→	Fe_2O_3

The **value as reducing agents** of the other substances mentioned may be more clearly recognized by considering their decomposition products and the way in which they oxidize. Substances containing carbon, hydrogen and oxygen usually oxidize to water and carbon dioxid. Hence an amount of oxygen sufficient to convert any carbonaceous substance into H_2O and CO_2 may be taken as the amount of oxygen each will absorb.

Oxalic acid, $H_2C_2O_4$, will decompose into H_2O, CO_2 and CO. All of these compounds are oxidized as completely as possible with the exception of CO. One molecule of oxalic acid is, therefore, equivalent to 1CO.

Tartaric acid, $H_6C_4O_6$, may break down into $3H_2O + 3CO + C$. One molecule is, therefore, equivalent to $3CO + C$.

One molecule of **alcohol,** H_6C_2O, is equivalent as a reducing agent to 2H, since after two hydrogen atoms have been oxidized away from each molecule, the residue, H_4C_2O, aldehyde, is volatile and is removed from the sphere of action.

Hydrosulfuric acid, H_2S, may be broken down into 2H and S. When oxidized by permanganate, the sulfur is largely converted into SO_3, but with other oxidizing agents the main reaction is the oxidation of the hydrogen, the sulfur not being attacked readily.

Sulfurous acid, H_2SO_3, decomposes into H_2O and the acid anhydrid, SO_2.

Thiosulfuric acid, $H_2S_2O_3$, will decompose into $H_2SO_3 + S$. Both the SO_2 and the S are readily oxidized to SO_3. For the oxidizing action of iodin see page 189.

Thiocyanic acid, HSCN, is equivalent to $HCN + S$, the sulfur being readily oxidized to SO_3.

Hydriodic acid, HI, will decompose into $H + I$. Iodin is not ordinarily oxidized, since it is insoluble in water and volatile at 100°. Hydriodic acid is equivalent to 1H, therefore.

Similarly **Hydrobromic acid,** HBr, and **Hydrochloric acid,** HCl, are each equivalent to 1H for each molecule of acid used.

These facts may be better appreciated when arranged in the following table of equivalents:

Hydriodic acid, HI,	is equivalent to	H
Hydrobromic acid, HBr,	"	H
Hydrochloric acid, HCl,	"	H
Alcohol, H_6C_2O,	"	2H
Hydrosulfuric acid, H_2S,	"	$2H + S$
Sulfurous acid, H_2SO_3,	"	SO_2
Thiosulfuric acid, $H_2S_2O_3$,	"	$SO_2 + S$
Thiocyanic acid, HSCN,	"	$HCN + S$
Oxalic acid, $H_2C_2O_4$,	"	CO
Tartaric acid, $H_6C_4O_6$,	"	$3CO + C$

From the table of oxygen equivalents of the various oxidizing agents it is seen that several different substances are of the same value, molecule for molecule. Two atoms of chlorin have the same oxidizing power as two atoms of iodin, since each is equivalent to one atom of oxygen. It is not to be inferred from this, however, that one substance gives as general satisfaction as an oxidizing agent as the other. Iodin is an inert element compared with chlorin, and while the latter, because of its greater chemical activity, will attack and oxidize almost any substance, iodin has a very limited application. Chlorin is, therefore, a much better oxidizing agent for general use than iodin.

Similarly hydrochloric and hydriodic acids have the same values as reducing agents, one molecule of each being equivalent to one atom of hydrogen. Hydrochloric acid, however, is a very stable compound and does not part with its hydrogen readily. Except in the presence of the very strongest oxidizing agents, hydrochloric acid shows no reducing properties at all. Hydriodic acid, on the other hand, gives up its hydrogen with especially great readiness. Hence hydriodic acid is a much better reducing agent for ordinary purposes than hydrochloric acid.

Much of the **value of oxidizing and reducing agents** depends on factors other than their oxygen or hydrogen equivalents. Chief among these factors are the chemical activity and stability of the substances. *Bodies which readily decompose into active decomposition products will be the best oxidizing and reducing agents.* Substances of this character are known as strong reagents. Nitric, dichromic, permanganic and chloric acids together with chlorin and bromin are strong oxidizing agents while iodin is especially weak. Nascent hydrogen, hydrogen sulfid, hydriodic and sulfurous acids are strong reducing agents while hydrobromic acid and alcohol are weak.

By reference to the tables of values already given, the relative **amounts of oxidizing and reducing agents which will interact** may be determined. As an illustration of their use, let the equation for the oxidation of **oxalic acid by permanganate** in acid solution be required. Two molecules of permanganic acid are equivalent to five atoms of oxygen. Each molecule of oxalic acid is equivalent to one molecule of carbon monoxid which will absorb one atom of oxygen and become carbon dioxid. Therefore, five molecules of oxalic acid will be oxidized by two molecules of permanganic acid. The essential reaction is:

$$5CO + Mn_2O_7 \rightarrow 5CO_2 + 2\mathbf{MnO}$$

The reaction may be completed by further consultation of the tables and the application of the general principles of chemistry. Instead of the equivalent CO, $H_2C_2O_4$ will appear on the left side which will introduce on the right side $1H_2O + 1CO_2$ additional for each molecule of oxalic acid which is oxidized. In the presence of acid MnO will dissolve and form a salt, hence if H_2SO_4 be the acid present, enough of it must appear in the reaction to unite with the MnO. The complete reaction becomes, then:

$$5H_2C_2O_4 + 2HMnO_4 + 2H_2SO_4 \rightarrow 10CO_2 + 8H_2O + 2MnSO_4$$

If potassium permanganate is used instead of permanganic acid, as is usually the case, additional sulfuric acid must appear in the equation sufficient to unite with the potassium oxid present, for $2KMnO_4$ is equivalent to $K_2O + Mn_2O_7$. One molecule of sulfuric acid will be needed for this purpose which will form potassium sulfate and water. Using potassium permanganate the complete reaction becomes:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \rightarrow 10\mathit{CO_2} + 8H_2O + 2MnSO_4 + K_2SO_4$$

The interaction between **dichromic acid and hydrogen sulfid** may be readily expressed by an equation when it is known that dichromic acid does not carry the oxidation any farther than water and free sulfur. H_2S is equivalent to $2H + S$. If S is not oxidized further, H_2S becomes equivalent to 2H. Two molecules of chromic anhydrid are equivalent to one molecule of the basic chromium trioxid, Cr_2O_3, $+ 3O$. Since 2H unite with 1O, the essential reaction is:

$$2CrO_3 + 3\mathit{H_2S} \rightarrow \mathbf{Cr_2O_3} + 3H_2O + 3\mathbf{S}$$

If the reaction takes place in a solution of dilute hydrochloric acid, as is usually the case, the complete reaction becomes:

$$H_2Cr_2O_7 + 3\mathit{H_2S} + 6HCl \rightarrow 2CrCl_3 + 7H_2O + 3\mathbf{S}$$

One of the common reactions of qualitative analysis is the oxidation of **arsenic sulfid, $\mathbf{As_2S_5}$, with nitric acid.** Since this substance is not soluble in water or acids, it is necessary to oxidize it to get it into solution. The reaction,

$$As_2O_5 + 5H_2S \rightarrow \mathbf{As_2S_5} + 5H_2O$$

shows arsenic sulfid to be a salt of hydrogen sulfid. In this compound arsenic shows its highest valence and can not be oxidized further. The oxidation of As_2S_5 is, therefore, the oxidation of H_2S alone. Under the conditions of the experiment much of the sulfur remains unoxidized; hence H_2S is here equivalent as a reducing agent to 2H. $5H_2S$ will require 5O. N_2O_5 is equivalent to 3O. The essential equation is, therefore:

$$5N_2O_5 + (3 \times 5 = 15)\mathit{H_2S} \rightarrow 5\mathit{N_2O_2} + 15\mathbf{S} + 15H_2O$$

Completing the reaction, we have:

$$(5 \times 2 = 10)HNO_3 + 3\mathit{As_2S_5} + (3 \times 5 = 15)H_2O \rightarrow$$
$$5\mathit{N_2O_2} + 15\mathbf{S} + 3As_2O_5 + 20H_2O$$

Since, however, $15H_2O$ or more appears on both sides of the equation, this quantity may be substracted from each side and the equation simplified as follows:

$$10\mathrm{HNO}_3 + 3\mathbf{As}_2\mathbf{S}_5 \rightarrow 5\mathit{N}_2\mathit{O}_2 + 15\mathbf{S} + 3\mathrm{As}_2\mathrm{O}_5 + 5\mathrm{H}_2\mathrm{O}$$

Many of the oxidation and reduction reactions applied in qualitative analysis take place in water solutions, hence are ionic reactions. **Ionic equations** may be readily written to express them. For the interaction of oxalic acid with permanganate:

$$2\overset{+}{\mathrm{K}} + 2\overset{-}{\mathrm{Mn}}\mathrm{O}_4 + (5 \times 2 = 10)\overset{+}{\mathrm{H}} + 5\overset{=}{\mathrm{C}}_2\mathrm{O}_4 + (3 \times 2 = 6)\overset{+}{\mathrm{H}} + 3\overset{=}{\mathrm{S}}\mathrm{O}_4 \rightarrow$$
$$2\overset{++}{\mathrm{Mn}} + 2\overset{+}{\mathrm{K}} + 3\overset{=}{\mathrm{S}}\mathrm{O}_4 + 10\mathit{CO}_2 + 8\mathrm{H}_2\mathrm{O}$$

By collecting common terms and eliminating common factors from both sides, the equation becomes the simplest expression for the reaction.

$$2\overset{-}{\mathrm{Mn}}\mathrm{O}_4 + 5\overset{=}{\mathrm{C}}_2\mathrm{O}_4 + 16\overset{+}{\mathrm{H}} \rightarrow 2\overset{++}{\mathrm{Mn}} + 10\mathit{CO}_2 + 8\mathrm{H}_2\mathrm{O}$$

For dichromic and hydrosulfuric acids the equation is:

$$2\overset{+}{\mathrm{H}} + \overset{=}{\mathrm{Cr}}_2\mathrm{O}_7 + (3 \times 2 = 6)\overset{+}{\mathrm{H}} + 3\overset{=}{\mathrm{S}} + 6\overset{+}{\mathrm{H}} + 6\overset{-}{\mathrm{Cl}} \rightarrow$$
$$2\overset{+++}{\mathrm{Cr}} + 6\overset{-}{\mathrm{Cl}} + 3\mathbf{S} + 7\mathrm{H}_2\mathrm{O}$$

The simplified expression is:

$$\overset{=}{\mathrm{Cr}}_2\mathrm{O}_7 + 3\overset{=}{\mathrm{S}} + 14\overset{+}{\mathrm{H}} \rightarrow 2\overset{+++}{\mathrm{Cr}} + 3\mathbf{S} + 7\mathrm{H}_2\mathrm{O}$$

For nitric acid and arsenic pentasulfid the equation is:

$$10\overset{+}{\mathrm{H}} + 10\overset{-}{\mathrm{N}}\mathrm{O}_3 + 3\mathbf{As}_2\mathbf{S}_5 \rightarrow 5\mathit{N}_2\mathit{O}_2 + 15\mathbf{S} + 5\mathrm{H}_2\mathrm{O}$$

All of these equations show the disappearance of hydrogen ions during oxidation reactions. The following ionic equations show the decrease in hydroxyl ions during reduction:

$$\overset{++++}{\mathrm{Sn}} + 2\mathrm{H}\text{—} \quad + 2\ \overset{-}{\mathrm{O}}\mathrm{H} \rightarrow \overset{++}{\mathrm{Sn}} + 2\mathrm{H}_2\mathrm{O}$$
$$2\overset{+++}{\mathrm{Fe}} + \mathrm{H}_2\mathrm{S} + 2\ \overset{-}{\mathrm{O}}\mathrm{H} \rightarrow 2\overset{++}{\mathrm{Fe}} + \mathbf{S} + 2\mathrm{H}_2\mathrm{O}$$

In qualitative analysis these elements are not ordinarily reduced in alkaline solution but rather in acid. Under these conditions reduction causes the production of hydrogen ions which may be considered equivalent to a decrease in hydroxyl ions since on neutralization each disappears. The following equations indicate the nature of the reduction process in acid solutions:

$$\overset{++++}{\mathrm{Sn}} + 4\overset{-}{\mathrm{Cl}} + 2\mathrm{H}— \rightarrow \overset{++}{\mathrm{Sn}} + 4\overset{-}{\mathrm{Cl}} + 2\overset{+}{\mathrm{H}}$$

Striking from each side of the equation the common term $4\overset{-}{\mathrm{Cl}}$, the expression becomes:

$$\overset{++++}{\mathrm{Sn}} + 2\mathrm{H}— \rightarrow \overset{++}{\mathrm{Sn}} + 2\overset{+}{\mathrm{H}}$$

Ferric iron reduced by hydrogen sulfid in acid solution may be represented as follows:

$$2\overset{+++}{\mathrm{Fe}} + H_2S \rightarrow 2\overset{++}{\mathrm{Fe}} + 2\overset{+}{\mathrm{H}} + \mathbf{S}$$

These equations indicate clearly that in solutions of salts of the metals the essential feature of **oxidation is an increase in the positive charge on the kathions.** Reduction correspondingly reduces this charge. The only difference between iron in the ferric state and iron in the ferrous state is that ferric ions have three unit charges while ferrous ions carry only two charges. The difference between a charge of four plus units and two plus units is the difference between stannic and stannous ions.

The interaction of oxidizing and reducing agents may be made to take place in the " **dry way** " by the application of heat. Reducing substances, such as tartaric and oxalic acids and other carbonaceous matter which interferes with the systematic analysis, are usually oxidized and burned up completely by fusion with ammonium, potassium or other salt of nitric acid. Other oxidizable substances, if present, are oxidized as well. Sulfids are changed to sulfates, chromium compounds to chromates and manganese salts to the green manganates. (See page 263.)

Many substances may be oxidized by heating in the air, especially if heated in the flame of a blowpipe. If ordinary illuminating gas, consisting essentially of hydrogen and carbon combined in various ways, be mixed with air as it emerges from the burner, complete combustion to carbon dioxid and water will ensue and the flame will be colorless. The flame from a blowpipe or Bunsen burner is of this character. Such a flame consists of three zones. An inner cone of unburned gas mixed with air is separated from the distinctly visible intermediate zone of blue flame by the surface where ignition begins. The hydrogen constituent of the gas burns immediately to water. Carbon burns first to carbon monoxid which at high temperatures is a strong reducing agent. Because of the presence of this substance, many oxids held in this intermediate zone are reduced, hence this portion is known as the **reducing flame.** Just beyond the tip of the distinct blue cone the temperature is highest and the best reduction effects are obtained here.

Carbon monoxid burns to carbon dioxid with a flame of characteristic blue color. The products of combustion, water and carbon dioxid, constitute the outer, scarcely visible zone of the flame. While still very hot these gases become mixed with oxygen from the air. Since oxygen at high temperatures is a very active agent, oxidation takes place very readily in this outer zone which is known as the **oxidizing flame.** Just beyond the point of the visible flame oxidation takes place most rapidly.

By heating a small particle of a substance before the blowpipe in the proper position in the flame, either oxidation or reduction may be effected. To obtain a satisfactory **blowpipe flame** the supply of air and gas entering a Bunsen burner should be cut down until a luminous flame not more than one inch high is obtained. By directing the blowpipe across the top of the burner and blowing gently yet steadily, a flame may be obtained in which the zones will be definitely separated and satisfactory results obtained.

PRELIMINARY EXAMINATION.

By the application of heat many solids exhibit phenomena so characteristic as to furnish evidence as to their nature. Consequently a series of very simple tests which may be quickly performed has been arranged in the hope that, by such a **preliminary examination,** information of value in the systematic analysis may be obtained. If the substance be homogeneous and fairly simple, a preliminary examination alone may be sufficient to determine its identity. The methods ordinarily used in making a preliminary examination are: (*a*) heating in a closed-tube, (*b*) heating with concentrated sulfuric acid, (*c*) heating on charcoal, (*d*) heating in a borax bead, (*e*) heating on a platinum wire in a Bunsen flame.

(*a*) **Heating in a closed-tube** consists in heating over a Bunsen burner a small amount of the substance under examination in a small tube of hard glass closed at *one* end. The object of the tube is to prevent as far as possible the oxidizing influence of the air in order that a reaction due to increase of temperature alone may be observed.

Under these conditions easily fusible substances melt and may often be volatilized completely, sometimes giving off very characteristic odors. Other substances do not melt under ordinary atmospheric pressure, but pass immediately into the gaseous state. Such substances are said to sublime. On cooling, the vapors condense to the solid form without passing through the intermediate liquid condition. Where it may be satisfactorily applied, **sublimation** offers an easy method of purification from non-volatile impurities.

Many difficultly fusible substances suffer a **change in color** on being heated, which in some cases is very characteristic.

Many substances suffer decomposition by heating before they become volatile or in some cases even before melting. Reactions in which certain of the decomposition products are volatile under the conditions of the experiment are most likely to take place, since a reversal of the reaction is prevented by the removal of the volatile constituents as fast as they are formed. Water, being very volatile, is one of the commonest decomposition products of high temperature reactions.

When heated sufficiently high, all **bases lose water and form oxids** of the metals which are generally quite stable and are not further decomposed.

Acids decompose into water and the anhydrid generally. Some anhydrids are very stable. Others are readily decomposed and break down still further.

As a rule, **salts decompose into acid anhydrids and oxids of the metals.**

In general, **the more stable the acid is, the more stable will the salts be.** Hypochlorous, nitrous, carbonic and sulfurous acids are all unstable at ordinary temperatures. At higher temperatures their salts are correspondingly unstable. Nitric, chloric and sulfuric acids are more stable than the last mentioned acids and their salts require correspondingly higher temperatures to decompose them. Finally, boric and phosphoric acids are very stable bodies and their salts are more resistant than others.

The salts of a given acid with the various metals possess varying degrees of stability. **The most stable salts are formed by the most strongly basic elements.** To illustrate, the carbonates of ferric iron, chromium, tin, arsenic and antimony are not known since they are unstable at ordinary temperatures. The carbonates of mercury, copper, lead, magnesium and calcium show increasing stability, but they are all decomposed at a dull red heat. Strontium and barium carbonates require the highest temperature of the Bunsen flame while the carbonates of the alkali metals are undecomposed even at this temperature.

None of the oxids of the metals are particularly volatile, hence ammonia is the only basic salt-forming substance driven off by the heat of a Bunsen burner.* Most of the acid anhydrids are volatile at this temperature, silicic, boric and phosphoric anhydrids being the exceptions. Therefore, silicates, borates and phosphates generally are among the most **stable substances at high temperatures,** since neither acid nor basic oxid is volatile.

When an acid anhydrid is unstable and decomposes further, the decomposition temperatures of its salts do not show the wide variation noticed with the carbonates where the acid anhydrid is volatile only. All **nitrates** decompose readily at about the same temperature into a metallic oxid and the acid anhydrid, N_2O_5. The latter undergoes further decomposition in the manner set forth on page 150.

Fluorids, chlorids, bromids and iodids are very stable, although some salts are quite volatile.

The decomposition of the **salts of cyanogen acids** depends considerably on the nature of the metallic element present and will be treated in detail under appropriate headings when necessary.

Non-volatile **organic salts and acids** generally suffer far-reaching decompositions when heated, resulting in the separation of more or less free carbon. This process is known as **charring** or **carbonization.**

Certain of these phenomena are often observed by heating in a closed-tube. The characteristic changes and their significations are given on pages 243 and 244.

(*b*) By **heating with concentrated sulfuric acid** in a test-tube, decompositions analogous to those considered are brought about. Such reactions take place more rapidly and at lower temperatures in the presence of the acid than without this reagent. Decomposition products are frequently liberated which are easily recognized and afford indications as to the composition of the substances so treated. For characteristic decompositions see pages 245.

(*c*) **Heating on charcoal** may be any one of three processes, depending on the nature of the substance and the conditions of the experiments. (1) If the substance be not reactive at high temperatures, any change observed will probably be physical. Fusion, volatilization, change of color, formation of a sublimate condensing on the charcoal at a distance from the flame, all may be observed. (2) If the charcoal be simply used as a support, the substance may be oxidized. (3) If the substance is mixed with sodium carbonate, used as a flux and to protect from the action of the air, the charcoal may exert a reducing action, especially if some of it is finely powdered and mixed with the sodium carbonate. From basic oxids certain of the metals may be separated in this way. Characteristic phenomena and their indications may be found on pages 246 and 247.

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* Mercuric oxid may be decomposed and then volatilized by the heat of a Bunsen flame.

(*d*) **Heating in a borax-bead** before the blowpipe is a high temperature reaction frequently productive of very characteristic colors. On being heated, borax, $Na_2B_4O_7.10H_2O$, intumesces and loses its water of crystallization. It then fuses to a clear, colorless glass which has the power of dissolving metallic oxids. Borax may be considered as a compound of two molecules of sodium metaborate, $NaBO_2$, with one molecule of boric acid anhydrid, B_2O_3, the combination being so unstable under certain conditions that it readily breaks down into these components. There is, therefore, such a predominance of the acid constituent that when borax is heated with metallic oxids, the acid anhydrid unites with them to form metaborates of the metals. The reaction with cobalt is typical.

$$\mathbf{Na_2B_4O_7 + CoO \rightarrow 2NaBO_2 + Co(BO_2)_2}$$

The metaborates of certain of the heavy metals are very intensely colored, a mere trace of the oxid, or of a substance capable of breaking down into the oxid under the conditions of the experiment, being distinctly indicated by the borax bead test. The characteristic colors developed are given on page 247.

(*e*) The heat of the Bunsen flame is sufficient to volatilize the compounds of certain metals and to cause momentary decomposition, in some cases into the free metal. In this condition, many salts produce a distinct **coloration of the Bunsen flame** which is characteristic of the metallic component. (See page 245.)

Of the common salts chlorids dissociate most readily, hence it is advisable to **moisten with hydrochloric acid** a small portion of the finely powdered substance. The paste may be inserted in a small loop of platinum wire and heated just beyond the blue cone in a Bunsen flame.

The coloration produced by certain metals is so intense that the merest trace of their salts is sufficient to indicate their presence. Hence it is necessary that the platinum wire should be very clean. A satisfactory method of **cleaning a platinum wire** from anything which may contaminate it is to make a small borax bead and cause it to pass along the wire by holding it in such a position in the flame that the bead is heated on one side only. Under these conditions the bead will travel away from the flame along the wire and dissolve anything that may be present. By driving the bead to the end of the wire and heating strongly for a moment, the bead may be thrown off by a sharp jerk, leaving the wire free from everything except a small amount of borax. This may be removed by alternately dipping the wire in pure, dilute hydrochloric acid and heating until the sodium color is no longer evident.

The color produced by insignificant amounts of sodium is so intense as to mask very completely the indication given by relatively large amounts of potassium. For this reason the **detection of potassium in the presence of sodium** becomes difficult to the unaided eye. By the spectroscope each may be detected in the presence of the other, since each is indicated by separate and distinct lines. Without the spectroscope it is necessary to cut out the sodium indication by something which will absorb the yellow rays of light produced by it and at the same time transmit the blue rays produced by potassium.

The most satisfactory method of accomplishing this point is by the use of a bottle filled with blue dye of such strength that a strong sodium flame is invisible when viewed through this solution. This apparatus is known as a **potassioscope.** With its aid traces of potassium may be detected in the presence of quantities of sodium. By suitably choosing the dye, not only the sodium flame, but also the indication given by all other common elements except potassium may be absorbed and thus all possible confusion avoided. (See page 319.)

WEIGHTS AND MEASURES

The atoms and molecules which enter into and constitute chemical substances have different relative weights which may be ascertained readily. *The weight of the atom of hydrogen is taken as the unit for comparison* and the **atomic weight** of hydrogen is said to be 1. *That number is taken as the weight of any other atom which tells how many times heavier it is than the hydrogen atom;* thus oxygen is 16, sodium 23, sulfur 32 and chlorin 35.5. The atomic weights of the elements are given on page 324.

The weight of the molecule is equal to the sum of the weights of the atoms in it; thus the **molecular weight** of NaCl is 58.5; Na_2SO_4 is 142.

When *one gram of any substance* is taken *for each unit in its molecular weight,* this amount *is called a* **gram-molecule.** Thus 40 grams of NaOH constitutes a gram-molecule, for, since the atomic weight of sodium is 23, of oxygen 16, and of hydrogen 1, there are 40 units in the molecular weight. In the gram-molecule of NaOH there are 23 grams of sodium, 16 grams of oxygen and 1 gram of hydrogen. Since the molecular weight of H_2SO_4 is 98, in the gram-molecule of sulfuric acid there are 32 grams of sulfur, 64 grams of oxygen and 2 grams of hydrogen, making 98 grams in all.

Solutions containing a gram-molecule of a substance in a liter of solution are called **gram-molecular solutions.** *In a gram-molecule of all substances there is the same number of molecules* and in equal volumes of gram-molecular solutions there is the same number of molecules.

A molecule of one substance reacts usually with a single molecule of another substance or with some simple multiple of this proportion, as 1 : 2, 1 : 3, 1 : 4, 2 : 3, and similar ratios. Consequently *one* **gram-molecule** *of one substance* **reacts with** *a single* **gram-molecule** *of another substance or with some simple multiple of this ratio.* Thus 1 gram-molecule of the monoacid base, NaOH, is just sufficient to neutralize 1 gram-molecule of the monobasic acid, HCl. One gram-molecule of the dibasic acid, H_2SO_4, will require 2 gram-molecules of the monoacid base, NaOH, to neutralize it or 1 gram-molecule of the diacid base, $Ca(OH)_2$.

In a gram-molecule of any monobasic acid there is one gram of hydrogen capable of passing into the ionic condition and of being replaced by metal in the formation of salts. In a gram-molecule of any dibasic acid there are two grams of this hydrogen while a tribasic or tetrabasic acid contains three or four grams. One-half a gram-molecule of any dibasic acid contains as much hydrogen capable of passing into the ionic condition as a gram-molecule of any monobasic acid and is therefore **equivalent** to it as an **acid.** Similarly one-third of a gram-molecule of a tribasic acid and one-quarter of a gram-molecule of a tetrabasic acid are equivalent to a gram-molecule of any monobasic acid.

One gram-molecule of a monoacid base is just sufficient to completely neutralize one gram-molecule of a monobasic acid, hence the two quantities may be said to be equivalent. One **equivalent** of **salt** is formed by the union of one equivalent of acid and of base. One-half of a gram-molecule of a diacid base, one-third a gram-molecule of a triacid base and one-fourth of a gram-molecule of a tetracid base are **equivalent** to one gram-molecule of a monoacid **base.**

In this way a **system of equivalents** has been developed such that an equivalent of any substance is just sufficient to react completely with an equivalent of any other substance. *That amount is taken as the equivalent of any substance which will combine with or take the place of one gram of hydrogen.* Thus 35.5 grams of chlorin unite with 1 gram of hydrogen to form 36.5 grams of hydrogen chlorid. Therefore 35.5 grams of chlorin and 36.5 grams of hydrogen chlorid are the equivalents of 1 gram of hydrogen. 35.5 grams of chlorin may be replaced by 17 grams of hydroxyl, OH, to form water. 17 grams of the OH radicle is the equivalent of 1 gram of hydrogen. 1 gram of hydrogen may be replaced by 23 grams of sodium or 39 grams of potassium or 108 grams of silver, hence these amounts are all equivalents.

40 grams of calcium unite with 71 grams of chlorin. Since 35.5 grams of chlorin are equivalent to 1 gram of hydrogen, 71 grams are 2 equivalents. Then 40 grams of calcium is 2 equivalents also, and 20 grams of calcium is the equivalent of 1 gram of hydrogen.

In this way the **values of the equivalents** of each element and compound may be determined. *In general, the equivalent of an acid or base equals the gram-molecule divided by the basicity or acidity of the compound. The equivalent of an element is equal to the atomic weight divided by the valence. The equivalent of any compound is that part of a gram-molecule which contains one equivalent of the active agent.*

By the term **active agent** is understood that particular constituent of the compound which is the essential factor in the reaction under consideration. A compound containing several different elements in different proportions may be considered from the standpoint of each element in different reactions, hence its equivalent may vary. Potassium permanganate, $KMnO_4$, may act as a potassium salt. Under these conditions potassium is the essential factor. 39 grams of potassium are contained in 158 grams of permanganate and the gram-molecule would be the equivalent under these circumstances. Again, the compound may be used as a source for the divalent $\overset{++}{\mathrm{Mn}}$ ion. Manganese has an atomic weight of 55, hence its equivalent is 27.5 grams. Since the equivalent of manganese is contained in 79 grams of permanganate, the equivalent of permanganate regarded as a source for $\overset{++}{\mathrm{Mn}}$ ions is one-half the gram-molecule. On the other hand, from one gram-molecule of $KMnO_4$ 40 grams of oxygen are readily liberated. Since 8 grams of oxygen unite with 1 gram of hydrogen, 40 grams of oxygen is 5 equivalents. Considering oxygen as the active agent, one-fifth of a gram-molecule of permanganate is the equivalent of 1 gram of hydrogen.

If *a solution* be made *of such strength that in a litre of solution there is one equivalent of solute,* it *is known as a* **normal solution.** Solutions of this strength are designated by the capital letter N; of twice this strength by 2N; of ten times this strength by 10N; one-half or one-tenth this strength by N/2 or N/10. Equal volumes of normal solutions are just sufficient to react together completely. Thus 1 liter N NaOH or KOH or $Ca(OH)_2$ will just neutralize 1 liter of N H_2SO_4 or HNO_3 or HCl. 1 ccm. N NaCl solution will completely precipitate 1 ccm. N

$AgNO_3$ solution. 10 ccm. 2N Na_2CO_3 is just sufficient to react completely with 200 ccm. N/10 $CaCl_2$ solution.

For purposes of convenience in handling, **laboratory reagents** are generally[*] made up according to this method. The strengths of the ordinary reagents suitable for qualitative analysis are given on pages 313–320, also directions for preparing these solutions.

PART II

DESCRIPTIVE

The Classification of the Elements.

A detailed study of the elements and of the principal compounds formed by each reveals the fact that, while any given element is very unlike most others in nature and properties, it does show very close and striking similarity to a few of them. If a systematic consideration of the elements be taken up in the order of their increasing atomic weights, hydrogen being excluded since it does not resemble any other elementary substance, we begin with the rare element, helium, At. Wt. 4. This is chiefly remarkable for its inertness. No compounds of it are known. Since it does not seem to have the power to unite with other elements, its valence may be said to be zero. The second element is lithium, At. Wt. 7, a typical metal, forming many compounds in which it shows a valence of one. Its hydroxid acts as a very strong base. The third element is beryllium, At. Wt. 9, a divalent metal, uniting readily with other elements. Its hydroxid acts as a base, but it is not as strong as lithium hydroxid. Trivalent boron, with At. Wt. 11, is the fourth element. Here metallic properties have fallen off very materially while the characteristics of non-metallic, acid-forming elements begin to appear. Tetravalent carbon, At. Wt. 12, is the next element, showing acid-forming rather than base-forming properties. Next in order comes nitrogen, At. Wt. 14. It is a typical non-metallic element, forming compounds in which valences of three or five are shown. Oxygen, At. Wt. 16, next in order, possesses strong non-metallic properties and exhibits a valence of two (possibly four or six) in its compounds. Fluorin, At. Wt. 19, is the most non-metallic of all elements, forming compounds in which a valence of one is characteristic.

Although the atomic weights of these substances are not widely different, no one of the elements can be considered as resembling any of the others, and, while the properties of fluorin and lithium seem to be as different as is possible, yet, considering the whole series just mentioned, only a gradual change from the one to the other is to be noted.

Continuing the list, the next element is neon, At. Wt. 20, remarkably inert, forming no compounds and resembling helium so closely as to make a separation of them exceedingly difficult. The next member, sodium, At. Wt. 23, is a typical univalent metal. Its hydroxid is one of the strongest bases and, in every way, it resembles lithium very closely. Magnesium, At. Wt. 24, is a divalent metal resembling beryllium.

Aluminum, At. Wt. 27, is trivalent and analogous to boron, while silicon, At. Wt. 28, is tetravalent and like carbon. Phosphorus, At. Wt. 31, duplicates most of the compounds of nitrogen. Sulfur, At. Wt. 32, resembles oxygen and shows generally a valence of two or six. Chlorin, At. Wt. 35, possesses non-metallic properties in a very high degree, forms several of the strongest acids and shows, among others, characteristic valences of one and seven.

Considering the members of what may be termed this second series, we note similarity so close as to seem almost a duplication of the properties of the first series. The same change from strongly metallic to decidedly non-metallic properties, accomplished by a gradual gradation through intervening elements, is observed. No member of this series can be said to be like any other member, yet each is very like the corresponding member of the first series.

Continuing the consideration of the elements, the same variation and similarities are observed, for argon is like neon and helium, potassium like sodium and lithium, calcium like magnesium and beryllium, ect. In short, if the elements be arranged in series according to their increasing atomic weights, spaces being left in some instances for hypothetical elements as yet undiscovered, the elements will be found to arrange themselves in groups, each group containing elements which possess similar properties. From this it would seem that the properties of the elements depend in some way upon their atomic weights. An increase in atomic weight at first produces entirely different properties, but, after a period, gives rise to properties closely resembling those previously noted.

As first enunciated by Mendeleeff, this generalization, known as the **Periodic Law,** states that *the properties of the elements are periodic functions of their atomic weights.* That is, that the properties of the elements depend primarily on their atomic weights and that, when arranged in the order of their increasing atomic weights, elements of a certain type occur periodically.

The **Periodic System** is a method of classification arranging the elements into groups such that the members of each group show great chemical similarity to each other. At the top of each group as given in the chart, the principal valences of the elements in the group are shown by typical formulae, R standing for any element belonging to the group. The increase in valence from zero to four and the subsequent decrease in valence toward hydrogen is shown by the formulae for hydrogen compounds, while the steady increase in valence toward oxygen is indicated by the formulae for oxids.

Series.	Group 0.	Group 1. RH R_2O	Group 2. RH_2 RO	Group 3. RH_3 R_2O_3	Group 4. RH_4 RO_2
1	He 4	Li 7	Be 9	B 11	C 12
2	Ne 20	Na 23	Mg 24	Al 27	Si 28
3	Ar 40*	K 39	Ca 40	Sc 44	Ti 48
4		63 Cu	65 Zn	70 Ga	72 Ge
5	Kr 82	Rb 85	Sr 88	Yt 89	Zr 91
6		108 Ag	112 Cd	115 In	119 Sn
7	Xe 128	Cs 133	Ba 137	La 139	Ce 140
8		——	——	——	——
9	——	——	——	——	——
10		197 Au	200 Hg	204 Tl	207 Pb
11	——	——	Ra 225	——	Th 232

Certain very rare substances, at present thought to be elementary in character, weights, approximately determined, are: Praseodymium—140; Neodymium—144; Ytterbium—173.

* Probably incorrectly determined.

In a general way, each one of the groups of the periodic system may be said to possess certain group properties which are characteristic of each member in the group. Chief among these are the valence and the general character of the elements; *i. e.*, do the elements in any particular group act normally as strong acid-formers or strong base-formers, or are they of an intermediate nature?

Within each group, however, certain gradations are to be noted. The most important of these is the fact that as the atomic weight of the elements in any particular group increases, non-metallic properties grow less, while metallic properties increase. This holds true for all groups whether they be of a general acid-forming, base-forming or neutral character. Thus, in the strong base-forming group caesium, At. Wt. 133, is more metallic than lithium, At. Wt. 7. In the decidedly non-metallic halogen group, fluorin, At. Wt. 19, shows this non-metallic character in a much greater degree than does iodin, At. Wt. 127. In the intermediate fifth group, nitrogen, At. Wt. 14, is a typical acid-forming element while bismuth, At. Wt. 209, is typically metallic and a weak base-forming element.

As the atomic weight of the elements rises above fifty, a differentiation of the elements in each group according to two types is to be noted, and, while both types generally possess the group characteristics, they clearly differ from each other in many ways. Thus, in the sixth group, chromium, molybdenum, tungsten and uranium are quite different from oxygen, sulfur, selenium and tellurium, although all these elements may with propriety be classed in one group.

Group 5. RH_3 R_2O_5	Group 6. RH_2 RO_3	Group 7. RH R_2O_7	Group 8.			Series.
N 14	O 16	F 19				1
P 31	S 32	Cl 35				2
51 Va	52 Cr	55 Mn	Fe 56	Co 59	Ni 59	3
As 75	Se 79	Br 80				4
94 Nb	96 Mo	——	Ru 102	Rh 103	Pd 106	5
Sb 120	Te 127*	I 127				6
——	——	——	——	——	——	7
——	——	——				8
183 Ta	184 Wo	——	Os 191	Ir 193	Pt 195	9
Bi 209	——	——				10
——	238 U	——				11

are not placed in the table because of insufficient data. Their names and atomic Samarium—150; Gadolinium—156; Terbium—160; Erbium—166; Thulium—171;

* Probably incorrectly determined.

In accordance with the classification afforded by the Periodic System, the more commonly-occurring elements will be considered in detail.

Group 0.

Helium 4; Neon 20; Argon 39.9; Krypton 81.8; Xenon 128.

Of the substances included in this group, argon only is at all common. It occurs in the atmosphere to the extent of about one per cent. along with all the other members of this group, the latter being present in exceedingly minute quantities. All are gaseous and are characterized chiefly by their lack of chemical activity. Since it has not been found possible to make any of them enter into combination with any other substance, they may be said to have a valence of zero. Only one type of element within this group has been discovered. Because of their rarity and lack of compounds, these elements will not be considered in detail.

Group 1; First Type.

Lithium 7; **Sodium 23**; **Potassium 39.2**; Rubidium 85.5; Caesium 132.9; **Ammonium.**

This group of alkali metals, as they are called, are soft, light, lustrous substances, possessing metallic properties in a marked degree. They are exceedingly reactive, tarnishing in the air and decomposing water with the liberation of hydrogen and the formation of hydroxids which are the strongest of bases. Their compounds are generally white in color and very soluble, and the group is to be remembered as the only one forming soluble carbonates and phosphates. Unlike all other groups, the hydroxids and carbonates of these elements are not decomposed by heat and the only acid carbonates, known in the solid state, are those of the alkali metals. So closely do the different elements resemble each other that separations are oftentimes difficult. Heated in a Bunsen flame, however, their compounds produce very characteristic colors by which the elements may be detected and differentiated.

Ammonium hydroxid is known as the "volatile alkali" in distinction from the other "fixed alkalies," *i. e.*, non-volatile alkalies, just mentioned. Because its compounds possess properties very similar to those of potassium compounds, it will be considered along with these elements.

Because of the great solubility of the salts of the alkali metals, they are much used to introduce various anions into solutions containing the ions of other metals, for the purpose of bringing about reactions.

Rubidium and caesium are very rare and will not be considered in detail.

LITHIUM. Li — 7.

Lithium is a silver-white metal. It is the lightest of all solid substances and will float on the surface of petroleum and most other liquids which might be used to protect it from the action of the atmosphere. It resembles sodium (see page 67) so closely in all of its properties that a detailed description is unnecessary.

Lithium salts are generally white and, with the exception of the carbonate and phosphate, are readily soluble. They color a Bunsen flame carmine-red and may be detected with the spectroscope by a strong red line to the left of the sodium line. (See frontispiece.)

The only **lithium ion** known is **$\overset{+}{Li}$**, for the reactions of which any soluble salt will serve.

The **carbonate ion,** $\overset{=}{CO}_3$, precipitates, from concentrated solutions only, white Li_2CO_3 which is soluble in about 125 parts of H_2O.

The **phosphate ion,** **$\overset{\equiv}{PO}_4$**, precipitates from fairly concentrated solutions Li_3PO_4 which is soluble in about 2500 parts of H_2O. It readily forms supersaturated solutions from which precipitation is slow. That normal lithium phosphate may be precipitated from solution while the normal phosphates of the other alkali metals are hydrolyzed, is due to the fact that lithium is somewhat less basic than the other members of this group and its phosphates are much less soluble.

SODIUM (Natrium). Na — 23.

Sodium is a light, silver-white, soft metal. It is acted upon rapidly by the atmosphere, due chiefly to the water-vapor present, and requires to be kept under petroleum or some other liquid which does not attack it and will protect it from the air.

Heated in the air sodium burns with an intensely yellow flame, not to the oxid, Na_2O, but to the peroxid, Na_2O_2, a heavy straw-colored powder. When thrown into water it reacts violently according to the equation:

$$\mathbf{Na_2O_2} + H_2O \rightarrow 2NaOH + H_2O_2$$

Sodium peroxid in water is equivalent, therefore, to hydrogen peroxid in an alkaline solution.

Sodium acts as one of the strongest base-forming elements. It is violently attacked by all acids, the concentration of $\overset{+}{H}$ ions due to pure water being sufficient to cause a very vigorous action at ordinary temperatures. Hydrogen gas is liberated and sodium hydroxid formed, according to the equation:

$$2\mathbf{Na} + 2HOH \rightarrow 2NaOH + H_2$$

or writing an ionic equation:

$$2\mathbf{Na} + 2\overset{+}{H} + 2\ \overset{-}{OH} \rightarrow 2\overset{+}{Na} + 2\ \overset{-}{OH} + H_2$$

This reaction shows that water acts in this case as a typical acid. (See page 29.) It may be regarded, therefore, as the weakest of all acids, the metallic hydroxids being its salts.

So much energy is liberated when the metal passes into the ionic condition that its compounds are among the most stable salts known. They can be reduced to the metal in the "dry way" only and at an expense of considerable energy.

Sodium salts are generally colorless and, with the exception of a few of infrequent occurrence, are readily soluble.

Sodium salts color a Bunsen flame an intense yellow. In the spectroscope, sodium is indicated by a bright yellow line. (See frontispiece.) This reaction is so delicate that one-millionth of a milligram may be readily detected. Hence the sodium line is omnipresent and for this reason is used in locating the position of other lines in the spectrum.

The only known **sodium ion** is $\overset{+}{\mathbf{Na}}$, for the reaction of which any salt will serve.

The **hydroxyl ion, $\overset{-}{\mathrm{OH}}$,** added to a solution containing the $\overset{+}{\mathrm{Na}}$ ion, produces no precipitate, for NaOH is soluble in half its own weight of water. In dilute solutions, **sodium hydroxid** is almost completely dissociated and is one of the strongest bases known. For this reason it is much used to introduce $\overset{-}{\mathrm{OH}}$ ions into solutions containing the ions of other metals. The hydroxids of the metals generally are much less soluble than NaOH and, with the exception of the other alkali metals, the hydroxid (or oxid) of each may be precipitated by the addition of a solution of sodium hydroxid of suitable concentration. An excess of the reagent may cause the precipitate to dissolve, owing to the formation of soluble compounds. (See lead, antimony, arsenic, tin, aluminum, chromium, cobalt and zinc.)

This is due to the fact that the hydroxids of certain weak bases, which normally separate the hydroxyl ion to a slight extent, may also dissociate into $\overset{+}{\mathrm{H}}$ ions as well and act as weak acids. The high concentration of $\overset{-}{\mathrm{OH}}$ ions from a solution of NaOH or KOH represses the ionization of these hydroxids into $\overset{-}{\mathrm{OH}}$ ions and calls forth the separation of $\overset{+}{\mathrm{H}}$ ions instead. The strong base unites with the weaker hydroxid, now acting as an acid, to form a soluble salt. (See page 22.)

On standing in the air, sodium hydroxid, like all strong bases, absorbs carbon dioxid and passes into the carbonate.

$$2\mathrm{NaOH} + CO_2 \rightarrow \mathrm{Na_2CO_3} + \mathrm{H_2O}$$

For this reason NaOH always contains some $\mathrm{Na_2CO_3}$.

As "soda lye" or "caustic soda," sodium hydroxid finds many applications in the industries.

The **carbonate ion, $\overset{=}{\mathrm{CO}}_3$,** produces no precipitate, for $\mathrm{Na_2CO_3}$ is readily soluble. With the exception of the other alkalies, the carbonates of the metals are much less soluble than $\mathrm{Na_2CO_3}$ and, on the addition of this reagent, they (or their decomposition products) may be precipitated from solutions of their soluble salts (arsenic excepted, see page 50). Furthermore, since the sodium salts of all ordinary acids are soluble, by boiling any precipitated substance with $\mathrm{Na_2CO_3}$, the metallic elements may be obtained as carbonates or their decomposition products in a new precipitate while the acid radicles are separated as soluble sodium salts in the filtrate. Substances so treated are said to be *transposed.*

In solution, **sodium carbonate,** like all other soluble carbonates, is hydrolyzed appreciably (see page 29), and gives a basic reaction to litmus. Since its solution contains an appreciable concentration of $\bar{O}H$ ions, it may cause the precipitation of the hydroxid as well as the carbonate of any metal, provided these two compounds are soluble to about the same degree. Such is the case with several metals. (See lead, copper, bismuth, cobalt, nickel, zinc and magnesium.) On treating a solution of their soluble salts with any soluble carbonate, a precipitate falls, apparently consisting of a mixture of the hydroxids and carbonates of these metals. Such precipitates are usually called "basic carbonates." Since the composition of any of these precipitates varies much with the conditions under which it is brought down, it is questionable whether they are to be considered as true basic salts (see page 21) or simply mixtures.

From solution, Na_2CO_3 separates with ten molecules of water of crystallization. On gentle heating it becomes anhydrous, after which it may be fused without decomposition, in this respect differing from all other carbonates except those of the other fixed alkalies. (See page 54.)

When fused with 5–10 times its weight of Na_2CO_3, nearly every insoluble salt of other metals is transposed. A metathesis is started according to the following typical reaction:

$$\mathbf{Na_2CO_3 + PbSO_4 \rightarrow Na_2SO_4 + PbCO_3 \rightarrow PbO} + CO_2$$

This reaction is prevented from coming to equilibrium as long as an appreciable amount of $PbSO_4$ is present, on the one hand, by the large mass of Na_2CO_3 present, and, on the other hand, by the fact that lead carbonate* is decomposed as fast as formed. But little is actually known of the principles underlying such reactions, however, and although the laws governing reactions in solution seem to hold under these conditions also, they must be applied with caution because of the lack of definite data.

In making fusions, equal parts of Na_2CO_3 and K_2CO_3 are frequently used instead of Na_2CO_3 alone, inasmuch as the mixture fuses at a lower temperature than either pure salt. This phenomenon follows the general rule that the melting point of any substance is lowered by the admixture of any substance with it.

Under the names "soda," "sal soda" and "washing soda," Na_2CO_3 finds many applications.

* When insoluble salts of barium, strontium or calcium are fused in this manner, the reaction goes in the same direction forming carbonates, but the temperature of an ordinary fusion is not sufficient to decompose them into CO_2 and the oxids (see pages 99, 98, and 95).

The **nitrate ion, $\mathbf{\overset{-}{N}O_3}$**, causes no precipitation, for *all normal nitrates are readily soluble.* When heated, **sodium nitrate,** like all nitrates, decomposes into oxygen and oxids of nitrogen and of the metal (see page 150). For this reason it is much used as an oxidizing agent in reactions performed in the dry way. Heated gently with some mild reducing agent, it breaks down into sodium nitrite, $NaNO_2$, from which all other nitrites may be formed. As "Chili saltpeter" or "caliche," $NaNO_3$, is used extensively in making HNO_3, KNO_3 and in fertilizers.

The **sulfid ion, $\mathbf{\overset{=}{S}}$,** causes no precipitate, for the alkaline sulfids are readily soluble.

The **sulfate ion, $\mathbf{\overset{=}{S}O_4}$**, causes no precipitate, for Na_2SO_4 is readily soluble. From solutions, it crystallizes at ordinary temperatures with ten molecules of water and is known as "Glauber's salt." It is much used in the manufacture of "soda" and glass.

The **chromate ion, $\mathbf{C\overset{=}{r}O_4}$**, causes no precipitate. Since $Na_2CrO_4 \cdot 10H_2O$ is very deliquescent as well as very soluble, it can not be easily preserved, hence the potassium salt, K_2CrO_4, is more often used for the purpose of introducing $C\overset{=}{r}O_4$ ions into solutions containing metallic ions.

For similar reasons $K_2Cr_2O_7$ is preferable to $Na_2Cr_2O_7 \cdot 2H_2O$ for general laboratory use.

The **chlorid ion, $\mathbf{\overset{-}{C}l}$,** produces no precipitate, for the halids are all soluble, increasing in degree as the atomic weight of the halogen rises (see table, page 71). From hot solutions all crystallize anhydrous.

Sodium cyanid, NaCN, is very soluble and very deliquescent.

The **phosphate ion, $\mathbf{P\overset{\equiv}{O}_4}$**, unites with the $\overset{+}{N}a$ ion to form soluble salts of three distinct types. Tertiary sodium phosphate, Na_3PO_4, the normal salt, is formed only in the "dry way" and, when put into solution, hydrolyzes largely into the secondary salt, Na_2HPO_4, and NaOH, for the solution reacts strongly alkaline and crystallizes out $Na_2HPO_4.12H_2O$. This acid disodium phosphate, the secondary salt, is the substance to which reference is made when the term, "sodium phosphate," is used. To such a slight degree does phosphoric acid, H_3PO_4, separate all three of its hydrogen atoms as ions (see page 155) that the reaction to litmus of this acid salt is not what would naturally be expected, for hydrolysis of Na_2HPO_4 into NaH_2PO_4 and NaOH puts more $\overset{-}{O}H$ ions into solution than the number of $\overset{+}{H}$ ions formed by dissociation. Hence it has a slight basic reaction to litmus.

The **acid pyroantimonate ion, $\mathbf{H_2\overset{=}{S}b_2O_7}$**, produces, in concentrated neutral solutions, a white crystalline precipitate of $Na_2H_2Sb_2O_7$, which is soluble in about 400 parts of H_2O. None of the other alkalies give a similar reaction. Metals other than the alkalies must be absent, as they generally produce amorphous precipitates. This is the only form in which sodium may be separated by precipitation in aqueous solution from the other alkali metals. The method is scarcely to be recommended for general use, as the solution of the precipitating reagent, $K_2H_2Sb_2O_7$, must be prepared fresh for each test.

Inasmuch as the anions formed by the various acids are frequently introduced into solutions by means of their sodium salts, a list of the salts of the commoner acids is appended together with a statement of some of their properties, *i. e.*, color, character, approximate solubility and the formula for the ordinary salt.

Acid.	*Formula.*	*Color.*	*Character.*	*Solubility.**
Acetic	$Na(C_2H_3O_2).3H_2O$	White	Efflorescent	3
Arsenic	$Na_2HAsO_4.12H_2O$	White	Efflorescent	1.75
Arsenous (meta)	$NaAsO_2$	White	Poor crystals	Very sol.
Boric (tetra)	$Na_2B_4O_7.10H_2O$	White	Efflorescent	14
Carbonic	$Na_2CO_3.10H_2O$	White	Efflorescent	1.1
Carbonic, anhydrous	Na_2CO_3	White	Stable	5
Chloric	$NaClO_3$	White	Deliquescent	3
Chromic	$Na_2CrO_4.10H_2O$	Yellow	Deliquescent	0.1
Chromic (pyro)— "dichromic"	$Na_2Cr_2O_7.2H_2O$	Red	Deliquescent	0.9
Cyanic	$NaOCN$	White	Stable	Sol.
Ferricyanic	$Na_3(FeC_6N_6).H_2O$	Red	Deliquescent	5
Ferrocyanic	$Na_4(FeC_6N_6).12H_2O$	Yellow	Efflorescent	4.5
Hydrobromic	$NaBr$	White	Stable	1.15
Hydrochloric	$NaCl$	White	Stable	3
Hydrocyanic	$NaCN$	White	Deliquescent	Very sol.
Hydrofluoric	NaF	White	Stable	25
Hydriodic	NaI	White	Stable	0.6
Hydrosilicofluoric	Na_2SiF_6	White	Stable	150
Hydrosulfuric	Na_2S	Straw	Deliquescent	Sol.
Hypochlorous	$NaOCl$	White	Known only in solution	
Nitric	$NaNO_3$	White	Deliquescent	1.2
Nitrous	$NaNO_2$	Straw	Stable	1
Oxalic	$Na_2C_2O_4$	White	Stable	30
Perchloric	$NaClO_4$	White	Deliquescent	Very sol.
Permanganic	$NaMnO_4$	Purple	Deliquescent	Very sol.
Phosphoric	$Na_2HPO_4.12H_2O$	White	Efflorescent	10
Silicic (meta)	Na_2SiO_3	White	Stable	Very sol.
Sulfuric	$Na_2SO_4.10H_2O$	White	Efflorescent	2
Sulfurous	$Na_2SO_3.8H_2O$	White	Efflorescent	4.3
Thiocyanic	$NaSCN$	White	Deliquescent	Very sol.
Thiosulfuric	$Na_2S_2O_3.5H_2O$	White	Efflorescent	1.5
Tartaric	$Na_2(C_4H_4O_6).2H_2O$	White	Stable	2.5

* The solubility is expressed in grams or cubic centimeters of water necessary to dissolve one gram of the salt.

POTASSIUM (Kalium). K — 39.2.

Potassium is a soft, silvery metal with a bluish tint, in its properties and reactions closely resembling sodium. (See page 67.)

Potassium salts are generally colorless and usually somewhat less soluble than the corresponding sodium compounds.

Potassium salts give to a Bunsen flame a very characteristic color which is usually described as lavender or violet. Spectroscopically examined, the flame shows a red line considerably to the left of the sodium line and a violet line far to the right at the other end of the spectrum (see frontispiece). These lines are often detected with some difficulty by the untrained observer.

The only known **potassium ion** is $\overset{+}{\mathbf{K}}$, for the reactions of which any of the more soluble salts will serve. The compounds of potassium so closely resemble those of sodium that the more important differences only will be considered.

Potassium hydroxid, KOH, is possibly a trifle more strongly basic than sodium hydroxid. For most analytical reactions these reagents may be used interchangeably. As "potash lye" or "caustic potash," it finds less extensive application in the industries than does "caustic soda."

Potassium carbonate, $\mathbf{K_2CO_3}$, or "potash," is deliquescent, absorbing moisture readily from the air, unlike Na_2CO_3.

Potassium nitrate, $\mathbf{KNO_3}$, "saltpeter," unlike the sodium salt, is not deliquescent and, therefore, is used in the manufacture of explosives.

Potassium cyanid, KCN, is more commonly used in the extraction of gold and as a bath in electroplating with the precious metals than is the sodium salt.

Potassium sulfate, $\mathbf{K_2SO_4}$, crystallizes anhydrous from its solutions. The acid salt, $KHSO_4$, melts at 200°, losing water and changing into the pyrosulfate, $K_2S_2O_7$. On further heating this compound breaks up into the normal sulfate, K_2SO_4, and SO_3. Since nascent sulfur trioxid, thus formed, acts vigorously upon many compounds, fusion with acid potassium sulfate is used to decompose silicates and other compounds not readily attacked by acids.

Potassium chromate, $\mathbf{K_2CrO_4}$, as well as the **dichromate, $\mathbf{K_2Cr_2O_7}$**, crystallize anhydrous from their solutions. They are stable under ordinary conditions and, therefore, readily preserved. They are the reagents ordinarily used for introducing $\mathrm{C\overline{r}O_4}$ and $\mathrm{C\overline{r_2}O_7}$ ions into solution.

Potassium chlorate, $\mathbf{KClO_3}$, breaks down readily on heating into KCl and oxygen, hence is much used as an oxidizing agent, finding especial application in matches and pyrotechnics. On gentle heating, it loses part only of its oxygen, forming, at first, potassium perchlorate, $KClO_4$, according to the reaction:

$$2\mathbf{KClO_3} \rightarrow \mathbf{KClO_4} + O_2 + \mathbf{KCl}$$

Since $KClO_4$ is soluble in about 50 parts of H_2O, whereas $NaClO_4$ is much more soluble, a partial precipitation of $KClO_4$ may be obtained by treating a concentrated solution containing the $\overset{+}{K}$ ion with a saturated solution of $NaClO_4$. The precipitation is made more complete by the addition of alcohol.

Potassium tartrate, $K_2(C_4H_4O_6)$, is readily soluble. Acid potassium tartrate, $KH(C_4H_4O_6)$, requires about 90 parts of H_2O to dissolve it. In 50 per cent. alcohol, however, it is quite insoluble. The precipitation must be made in a solution slightly acid with acetic or some other weak acid, for the salt is soluble in the strong acids and in alkalies, in the latter case forming the readily soluble normal salt. Other than alkali metals must be absent, as they form insoluble precipitates under the same conditions. The ammonium ion, $\overset{+}{NH_4}$, if present, will give a similar precipitate but, on ignition, will be driven off entirely whereas the potassium salt will be changed to the carbonate as is the rule with salts of organic acids generally.

$$2\mathbf{KH(C_4H_4O_6)} + 5O_2 \rightarrow \mathbf{K_2CO_3} + 5H_2O + 7CO_2$$

"Rochelle salt," $KNa(C_4H_4O_6).4H_2O$, is soluble in 15 parts of H_2O.

Potassium platinic-chlorid, K_2PtCl_6, soluble in about 100 parts of H_2O, is precipitated as a yellow crystalline precipitate from concentrated solutions containing the $\overset{+}{K}$ ion by the addition of H_2PtCl_6. In alcohol it is much less soluble. The customary method of procedure is to evaporate almost to dryness the solution containing the $\overset{+}{K}$ and $\overline{Pt}Cl_6$ ions. Extraction with alcohol dissolves the soluble portion of the residue, leaving behind the potassium salt. The ammonium ion, $\overset{+}{NH_4}$, if present, gives a similar precipitate but, on ignition, is decomposed and the ammonium radicle completely driven off. Potassium platinic-chlorid, on ignition, is decomposed and leaves potassium chlorid and a residue of platinum according to the reaction:

$$\mathbf{K_2PtCl_6} \rightarrow 2\mathbf{KCl} + \mathbf{Pt} + 2Cl_2$$

Potassium cobalti-nitrite, $K_3Co(NO_2)_6$, is precipitated from very concentrated solutions containing the $\overset{+}{K}$ ion and acidified with acetic acid, by the addition of a solution of a cobaltous salt and solid sodium nitrite. Nitrous acid, HNO_2, set free by the acetic acid, first oxidizes the cobaltous ion, $\overset{++}{Co}$, to the cobaltic ion, $\overset{+++}{Co}$, which then unites with the $\overset{+}{K}$ ions and $\overset{-}{NO}_2$ ions to form the yellow $K_3Co(NO_2)_6$ (see page ——). The ammonium ion, $\overset{+}{NH}_4$, must be absent, as it forms a similar precipitate.

Potassium silicofluorid, K_2SiF_6, is a white crystalline salt, precipitated from slightly acid solutions containing the $\overset{+}{K}$ ion on the addition of the $\overset{=}{Si}F_6$ ion. It is much less soluble than the sodium salt, requiring about 825 parts of H_2O to dissolve. An equal volume of alcohol precipitates it from aqueous solution almost completely.

As potassium salts are frequently used to introduce anions into other solutions, a list of the ordinary salts of the commoner acids is appended, together with the chemical formula, color, character and approximate solubility of each.

Acid.	*Formula.*	*Color.*	*Character.*	*Solubility.**
Acetic	$K(C_2H_3O_2)$	White	Poor crystals	0.5
Arsenic	K_2HAsO_4	White	Stable	Sol.
Arsenous (meta)	$KAsO_2$	White	Stable	Sol.
Boric (meta)	KBO_2	White	Stable	Sol.
Carbonic	K_2CO_3	White	Deliquescent	0.9
Chloric	$KClO_3$	White	Stable	16
Chromic	K_2CrO_4	Yellow	Stable	1.75
Chromic (pyro)—"dichromic"	$K_2Cr_2O_7$	Red	Stable	10
Cyanic	KOCN	White	Stable	Sol.
Ferricyanic	$K_3(FeC_6N_6)$	Red	Stable	2.5
Ferrocyanic	$K_4(FeC_6N_6).3H_2O$	Yellow	Stable	3.5
Hydrobromic	KBr	White	Stable	1.5
Hydrochloric	KCl	White	Stable	3
Hydrocyanic	KCN	White	Deliquescent	Very sol.
Hydrofluoric	KF	White	Deliquescent	Very sol.
Hydriodic	KI	White	Stable	0.7
Hydrosilicofluoric	K_2SiF_6	White	Stable	825
Hydrosulfuric	K_2S	Straw	Deliquescent	Sol.
Hypochlorous	KClO	White	Known only in solution	
Nitric	KNO_3	White	Stable	3.3
Nitrous	KNO_2	Straw	Deliquescent	Sol.
Oxalic	$K_2C_2O_4.H_2O$	White	Stable	3
Perchloric	$KClO_4$	White	Stable	60
Permanganic	$KMnO_4$	Purple	Stable	15
Phosphoric	K_2HPO_4	White	Deliquescent	Very sol.
Silicic (meta)	K_2SiO_3	White	Stable	Very sol.
Sulfuric	K_2SO_4	White	Stable	10
Sulfurous	$K_2SO_3.2H_2O$	White	Deliquescent	1
Thiocyanic	KCNS	White	Deliquescent	0.5
Thiosulfuric	$K_2S_2O_3$	White	Deliquescent	Very sol.
Tartaric	$K_2(C_4H_4O_6).H_2O$	White	Stable	0.6

* The solubility is expressed in grams or cubic centimeters of water necessary to dissolve one gram of the salt.

AMMONIUM, NH_4.

Ammonium is a combination of nitrogen and hydrogen in the proportions of one volume of the former to four volumes of the latter. It exists in a great number of salts and other compounds in which it takes the place of a metal and shows the properties of a base-forming element. It is equally well known as a univalent kathion, separating at the negative pole in electrolysis as do the metals. It is not known free, however, for as soon as it is separated from any of its compounds, it decomposes into ammonia, NH_3, and hydrogen.

Ammonium salts resemble those of potassium very closely in their physical properties. Unlike the latter, they are all volatile, volatilization being accompanied by more or less decomposition which may be either temporary or permanent.

Salts of acids containing no oxygen are volatile (generally subliming) with dissociation into ammonia and the acid, which recombine on cooling.

$$\mathbf{NH_4Cl} \leftrightarrow NH_3 + HCl$$

Salts of acids containing oxygen which are not oxidizing agents split off the ammonia, gradually forming in the case of polybasic acids, acid salts first, which later decompose into ammonia and, generally, water and the acid anhydrid:

$$\mathbf{(NH_4)_2SO_4} \rightarrow NH_3 + \mathbf{H(NH_4)SO_4}$$
$$\mathbf{H(NH_4)SO_4} \rightarrow NH_3 + H_2O + SO_3$$

Salts of acids which are oxidizing agents decompose by an internal oxidation, the oxidizing and reducing agents both being contained in the compound itself. When ammonium nitrite is heated, the nitrite radicle oxidizes the ammonium radicle as indicated in the equation:

$$\mathbf{NH_4NO_2} \rightarrow 2\mathrm{H_2O} + N_2$$

Since all ammonium salts may be removed, if subsequently necessary, by moderate heating, they are much used for introducing various anions into solutions containing metallic ions.

Ammonium salts give no color to a Bunsen flame.

The only known **ammonium ion** is $\mathbf{N\dot{H}_4}$.

Ammonium hydroxid, NH_4OH, is known only in solution, for, on attempting to isolate it, decomposition into NH_3 and H_2O takes place. For this reason it is known as the "volatile alkali." The reaction between ammonia and water (see page 147) is a typical equilibrium reaction, as is shown by the equation:

$$NH_3 + H_2O \leftrightarrow NH_4OH$$

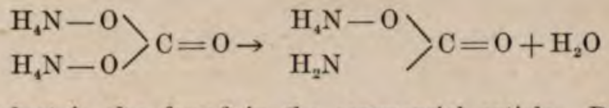
In solution, there is always a large portion of the gas dissolved in the water that is not united with it in the form of NH_4OH, hence the solution is frequently known as "ammonia water" as well as ammonium hydroxid. This free ammonia shows a special tendency to unite with various simple metallic ions to form complex ions.

Ammonium hydroxid separates the $\overset{-}{OH}$ ion to a considerably greater degree than do most metallic hydroxids. Compared with the alkaline hydroxids or even the hydroxids of the alkaline earth metals, it is only a weak base, however. A solution of potassium or sodium hydroxid of ordinary concentration contains more than sixty times as many $\overset{-}{OH}$ ions as a solution of ammonium hydroxid of the same concentration. Although these solutions are frequently used interchangeably for the introduction of $\overset{-}{OH}$ ions, it is only to be expected that the reactions would not be exactly the same in every case. (See different action of NH_4OH from KOH or NaOH on lead, tin and zinc hydroxids.)

Because sodium or potassium hydroxid dissociates so much more than ammonium hydroxid, salts of the latter are decomposed by the former reagents. Ammonium chlorid, as an example, on going into solution, dissociates almost completely, giving high concentrations of $\overset{+}{NH_4}$ and of $\overset{-}{Cl}$ ions. On the addition of KOH, high concentrations of $\overset{+}{K}$ and of $\overset{-}{OH}$ ions are introduced. Of the compounds which may be formed by these four different ions, all dissociate readily except NH_4OH. As this is formed, almost the whole of it remains undissociated and, therefore, cuts down the concentration of $\overset{+}{NH_4}$ and of $\overset{-}{OH}$ ions and removes them from the sphere of action. On warming such a solution, NH_4OH is decomposed and NH_3 passes off, leaving in solution only $\overset{+}{K}$ and $\overset{-}{Cl}$ ions to form KCl. This reaction is ordinarily used as a test for ammonium salts.

Ammonium carbonate, $(NH_4)_2CO_3$, is a white substance, soluble in about one part of water, used frequently as a reagent for the introduction of $\overset{=}{CO_3}$ ions into solutions containing metallic ions. Like all soluble carbonates, it hydrolyzes greatly into NH_4OH and H_2CO_3, both of which decompose into gaseous products. Hence a solution of ammonium carbonate contains NH_4OH and NH_3. Hydrolysis increases as the temperature is raised, hence by boiling, $(NH_4)_2CO_3$ may be entirely decomposed and removed from solution.

Ammonium carbonate splits off part of its ammonia even at ordinary temperatures and forms the acid salt. For this reason, the commercial product usually consists largely of acid ammonium carbonate, $H(NH_4)CO_3$. Ammonium carbonate also loses water readily forming ammonium carbamate according to the reaction:



$$\begin{matrix} H_4N-O \\ H_4N-O \end{matrix}\!\!>C=O \rightarrow \begin{matrix} H_4N-O \\ H_2N \end{matrix}\!\!>C=O+H_2O$$

This product is also found in the commercial article. By adding NH_4OH to a solution of commercial ammonium carbonate, however, no new substance is introduced and the acid salt is changed into the normal salt. Under the same conditions, also, the carbamate reverts to the carbonate.

Ammonium sulfid, $(NH_4)_2S$, may be formed as a white solid by bringing together NH_3 and H_2S gases at low temperatures. At ordinary temperatures, it is decomposed almost entirely into the constituents. In solution it is fairly stable when protected from the action of the atmosphere and of light. It is usually formed by saturating a volume of strong NH_4OH with H_2S which forms acid ammonium sulfid according to the reaction:

$$NH_4-OH+H-S-H \rightarrow NH_4-S-H+H_2O$$

By the addition of another volume of NH_4OH the normal salt is formed.

A fresh solution of $(NH_4)_2S$ is colorless and reacts alkaline, owing to hydrolysis into NH_4OH and H_2S. On standing in the light and air, it becomes yellow. The H_2S oxidizes slowly into H_2O and S, the latter substance dissolving in and reacting with $(NH_4)_2S$ to form some of the ammonium polysulfids, of which several are known, such as $(NH_4)_2S_2$, $(NH_4)_2S_4$ and so forth. A solution of these polysulfids is known as "yellow ammonium sulfid."

Ammonium sulfid is much used for the introduction of $\overset{=}{S}$ ions into solution because it furnishes a concentration of $\overset{=}{S}$ ions much greater than can be obtained by a saturated solution of H_2S. Moreover, it may be removed from solution simply by boiling, which is not true of the sulfids of the fixed alkalies.

Ammonium polysulfid is used to dissolve certain metallic sulfids (see antimony, arsenic, tin, gold and platinum) with which it unites to form soluble salts of thioacids.

Ammonium nitrate, NH_4NO_3, is a colorless, crystalline, deliquescent salt, soluble in about half its weight of water. On heating it decomposes, the nitric acid radicle oxidizing the ammonium radicle according to the equation:

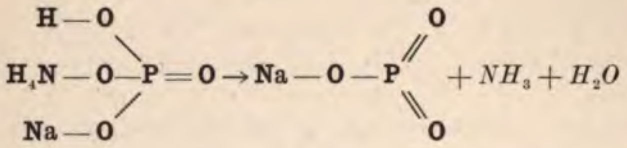
$$\mathbf{NH_4NO_3} \rightarrow N_2O + 2H_2O$$

In the presence of oxidizable material, the reaction does not form N_2O but N_2, the oxygen being taken up by the reducing agent. For this reason, it is often used in fusions to remove organic matter.

Ammonium acetate, $NH_4(C_2H_3O_2)$, is a colorless, crystalline deliquescent substance which is very soluble in water.

Ammonium chlorid, NH_4Cl, is a colorless, crystalline substance, soluble in 2.5 parts of H_2O. It unites with the salts of many metals to form double salts and is thus used to prevent the precipitation of metallic hydroxids by NH_4OH. (See magnesium, ferrous iron, cobalt, nickel, manganese and zinc. See also page 32.)

The **ammonium phosphates** are unimportant and closely resemble the salts of sodium and potassium. Microcosmic salt, $HNa(NH_4)PO_4.4H_2O$, is interesting because of its decomposition on heating into sodium metaphosphate, ammonia and water.



Sodium meta-phosphate is used frequently in fusions. Being a flux for all basic oxids, it leaves non-volatile, infusible, acid anhydrids, such as silica, undissolved and floating about in the clear melt. (See test for silicic acid, page 260.)

Ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, is a colorless crystalline body, soluble in about 23 parts of H_2O. It is generally used for the introduction of the oxalate ion into solutions.

A few less soluble complex salts of ammonium are known, such as the acid tartrate, platinic-chlorid and cobalti-nitrite. They resemble the potassium salts very closely. (See page 74.)

Ammonium silicofluorid, $(NH_4)_2SiF_6$, is soluble in about 5 parts of H_2O.

Ammonium molybdate, $(NH_4)_2MoO_4$, is a white crystalline substance without water of crystallization. It is soluble in about 5 parts of H_2O and is used as a reagent for detecting phosphoric and arsenic acids.

Group 1, Second Type.

Copper 63.6; Silver 107.9; Gold 197.2.

The members of this group are heavy, malleable metals which are good conductors of heat and electricity. They are found in nature both free and in combination with other elements and they are generally stable under ordinary conditions. They show but little tendency to pass into the ionic condition, hence are readily reduced from their compounds.

The group, as a whole, is not well characterized, however. The similarity of these elements to each other is not striking nor is the resemblance of this half to the other half of the same group sufficiently obvious. Copper and gold resemble elements in other groups quite closely and their right to a position in this group is not beyond question. Silver is a typical metal, acting as a fairly strong base-forming element. Its compounds are colorless and resemble those of the alkali metals and, like them, silver is consistently univalent.

COPPER (Cuprum). Cu — 63.6.

Copper is a rather soft, very malleable metal, possessing a characteristic red color. It tarnishes in moist air, forming a green basic carbonate sometimes known as verdigris. At higher temperatures, it unites readily with oxygen, giving rise to the black oxid, CuO.

The **metal** is attacked but little by HCl or by dilute H_2SO_4. This fact is readily explained by reference to the Potential Series (given on page 327), which shows that hydrogen passes into the ionic condition more readily than copper does. Consequently, when metallic copper is brought into contact with hydrogen ions, there is little tendency for the latter to give up their electric charges to the former and, therefore, the metal does not dissolve appreciably.

Oxidizing agents, however, convert the metal into the oxid and this will dissolve readily in acids. In this way the metal may be obtained in solution. Nitric acid acts both as an oxidizing agent and as an acid and for this reason readily dissolves those metals which, like copper, show less tendency to pass into the ionic condition than hydrogen does. Since hot, concentrated H_2SO_4 may act as an oxidizing agent (see page 187), it, also, will dissolve copper and similar metals.

By further reference to the Potential Series, it will be seen that most metals tend to pass into the ionic condition more readily than copper does. They are, therefore, said to be more *positive* metals. If one of these metals is introduced into a solution of a salt of copper, the charge passes from the copper ions to the metal. Copper is precipitated from solution in metallic form while the more positive metal passes into solution in the form of ions, as the equations indicate.

$$CuSO_4 + \mathbf{Zn} \rightarrow ZnSO_4 + \mathbf{Cu} \text{ or, simplified, } \overset{++}{Cu} + \mathbf{Zn} \rightarrow \mathbf{Cu} + \overset{++}{Zn}$$

Aluminum, iron and other metals will precipitate metallic copper from solutions of its salts because of the decidedly greater tendency of these metals to become ions.

All elements which, like copper, *show little tendency to pass into the ionic condition, are readily reduced from their salts to the metal and, conversely, those elements which pass readily into the ionic condition are reduced only with difficulty.*

When heated before the **blowpipe** with Na_2CO_3 on charcoal, all copper salts are reduced, but the metal shows little tendency to come together in a single globule. Under favorable conditions a minute red button may be formed without a coating on the charcoal. It is readily soluble in warm HNO_3, giving a blue solution, especially after the addition of NH_4OH.

Copper salts generally impart a green color to a Bunsen flame, very similar to the color produced by barium salts or boric acid. Cupric chlorid, however, gives a beautiful blue color which can hardly be mistaken. By moistening the substance to be tested with HCl and heating in a loop of platinum wire, the blue flame will usually be seen. A better way is to pass HCl* gas into one of the air-holes at the base of a Bunsen burner (which must not be made of brass) and heat the substance on a platinum wire in the flame, when, if copper be present, the blue flame will be observed.

Copper acts as a weak base-forming element. Its salts hydrolyze considerably and, in solution, exhibit a tendency to deposit insoluble basic salts. Two kinds of simple **copper ions** are known, the cupric ion, $\overset{++}{Cu}$, and the cuprous ion, $(\overset{+}{Cu})_2$. These resemble considerably the corresponding mercury ions (see page 107). There are also several complex ions, formed especially with NH_3 and the $\overset{-}{CN}$ ion, which will be considered in their proper places.

From the simple ions, two series of salts are formed which differ decidedly in their properties. The more stable cupric salts are colored usually blue or green, the nitrate, sulfate, acetate and chlorid being soluble. No cuprous salts of acids containing oxygen are known. The halids are colorless and highly insoluble in water. They tend to take up oxygen and pass into the higher form. The reactions of the two ions will be considered separately.

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* A little HCl generator suitable for this purpose may be made by heating concentrated HCl in a test-tube provided with a delivery-tube leading into one of the air-holes at the base of the Bunsen burner.

The Cupric Ion, $\overset{++}{Cu}$.

Cupric nitrate (or sulfate or chlorid) is a good source for $\overset{++}{Cu}$ ions. It is deep blue in color and crystallizes from solution with 3 or 6 H_2O. Both these substances are deliquescent and therefore can not be preserved as satisfactorily as salts which do not take up water vapor from the air. Both are extremely soluble. At 38°, $Cu(NO_3)_2.6H_2O$ will dissolve in its own water of crystallization.

The **hydroxyl ion, $\overset{-}{OH}$,** precipitates floccy, blue $Cu(OH)_2$, which tends to lose water slowly at ordinary temperatures and, on boiling, changes to black CuO.

In the presence of NH_3, the precipitate first formed is redissolved, owing to the formation of a complex cupric-ammonia ion, $\overset{++}{Cu}(NH_3)_4$, the compounds of which are soluble. This ion is somewhat unstable and the concentration of $\overset{++}{Cu}$ ions from its decomposition is sufficient to cause a partial precipitation of CuS when the $\overset{=}{S}$ ion is introduced. On the addition of acids the deep blue color characteristic of the $\overset{++}{Cu}(NH_3)_4$ ion disappears because of the decomposition of the complex ion caused by the union of the $\overset{+}{H}$ ion with the NH_3 to form the ammonium ion, $\overset{+}{NH_4}$. The addition of KCN bleaches the solution also, owing to the formation of colorless compounds as the following typical reactions indicate:

$$Cu(NH_3)_4SO_4 + 2KCN + 4H_2O \rightarrow CuC_2N_2 + K_2SO_4 + 4NH_4OH$$

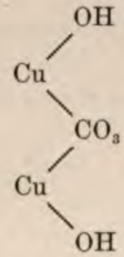
$$2CuC_2N_2 \rightarrow \mathbf{(CuCN)_2} + (CN)_2$$

$$\mathbf{(CuCN)_2} + 6KCN \rightarrow 2K_3(CuC_4N_4)$$

Cupric hydroxid dissolves in solutions of alkaline cyanids, forming complex cyanid ions.

In the presence of tartaric acid, citric acid, sugar or other organic substances containing hydroxyl radicles, no precipitation takes place when the $\overset{-}{OH}$ ion is introduced into solutions containing $\overset{++}{Cu}$ ions, owing to the formation of complex organic ions (see also page 117). By boiling with the simple sugars, the cupric portion of these ions is reduced to the cuprous condition and decomposition into the simple $(\overset{+}{Cu})_2$ ion takes place. In the presence of $\overset{-}{OH}$ ions, $(CuOH)_2$ forms but it is dehydrated immediately and red Cu_2O is precipitated. This reaction is used in estimating sugar in solution. (Fehling's Test.) Cane sugar must be inverted before it will cause reduction.

The **carbonate ion, $\overset{=}{\mathbf{CO}}_3$,** from alkaline carbonate solutions, causes a precipitation of a mixture of hydroxid and carbonate as a light blue precipitate. Since the composition of this substance is fairly constant, it is probable that a true basic salt is formed of the nature indicated by the formula:



(See page 21.)

The **sulfid ion, $\overset{=}{\mathbf{S}}$,** precipitates black CuS, insoluble in dilute acids and alkalies. Fairly strong HNO_3, when warm, dissolves it owing to oxidation to S (or H_2SO_4) and $Cu(NO_3)_2$. Copper sulfid is somewhat soluble in yellow ammonium sulfid, $(NH_4)_2S.xS$, less in yellow sodium sulfid, $Na_2S.xS$, and not soluble in colorless Na_2S (difference from HgS and Sb_2S_3 or Sb_2S_5. See pages 108, 167 and 168.) It is soluble in alkaline cyanids, forming soluble complex cyanids.

The **sulfate ion, $\overset{=}{\mathbf{SO}}_4$,** produces no precipitate, for the sulfate is soluble in about 4 parts H_2O at ordinary temperatures and less than 2 parts at 100°. From solutions, it crystallizes ordinarily in the form $CuSO_4.5H_2O$, but can be made to take up two additional molecules and conform to the type of the "vitriols" (see page 188). The ordinary salt is known commercially as "blue vitriol." Its blue color is lost when it is heated, for the anhydrous sulfate is dirty-white in color.

The **chromate ion, $\overset{=}{\mathbf{CrO}}_4$,** precipitates a yellow oxychromate, having the proportions represented by the formula, $3CuO.CrO_3.2H_2O$.

The **chlorid ion, $\overset{-}{\mathbf{Cl}}$,** causes no precipitation. The anhydrous salt is brown but it separates from solution in the form of green crystals having the composition $CuCl_2.2H_2O$. This salt is deliquescent and dissolves in less than its own weight of water.

The **iodid ion, $\overset{-}{\mathbf{I}}$,** probably forms cupric iodid at first, but this salt immediately breaks down into the insoluble, white cuprous iodid, $(CuI)_2$, with the separation of free iodin, which colors the solution brown.

$$2CuI_2 \rightarrow \mathbf{(CuI)_2} + 2I$$

The **cyanid ion, $\bar{\mathbf{C}}\mathbf{N}$,** forms the very unstable, yellow cupric cyanid at first, but this decomposes into the insoluble, white $(\mathrm{CuCN})_2$ and sets free CN. An excess of the cyanid causes the precipitate to dissolve, owing to the formation of complex cyanids (see reaction of $\bar{\mathrm{C}}\mathrm{N}$ ion on $(\overset{+}{\mathrm{Cu}})_2$ ion, page 84).

$$2\mathbf{Cu(CN)_2} \rightarrow \mathbf{(CuCN)_2} + 2CN$$

The **ferrocyanid ion, $(\mathbf{Fe}=\overline{\overline{\mathbf{C}}}_6\mathbf{N}_6)$,** precipitates gelatinous, mahogany-colored $\mathrm{Cu_2(Fe{=}C_6N_6)}$.

The Cuprous Ion, $(\overset{+}{\mathrm{Cu}})_2$.

Cuprous compounds may be considered as containing the element in the univalent condition. All of the compounds seem to have double molecules, as the formulae indicate. (Note similar doubled molecules of mercurous compounds, page 110.)

All compounds formed by the cuprous ion are so insoluble that no solution containing an appreciable concentration of $(\overset{+}{\mathrm{Cu}})_2$ ions can be made. The cuprous halids dissolve readily in their respective acids, however, forming complex cuprous-halogen acids of the type $\mathrm{H_2CuCl_3}$, $\mathrm{H_2CuBr_3}$, $\mathrm{H_2CuI_3}$, which dissociate into the complex ions $\mathrm{C\bar{u}Cl_3}$, $\mathrm{C\bar{u}Br_3}$ and $\mathrm{C\bar{u}I_3}$. If such a solution be diluted, the complex ions decompose into simple ions and the colorless salts, $(\mathrm{CuCl})_2$, $(\mathrm{CuBr})_2$ and $(\mathrm{CuI})_2$, are precipitated. They will dissolve in $\mathrm{NH_4OH}$, forming complex ammonia salts which, like most cuprous compounds, are colorless and give colorless solutions. Oxygen is quickly absorbed, however, and the deep blue color of the cupric-ammonia compounds appears at once.

A solution of a cuprous halid containing only sufficient acid to prevent precipitation of the salt will serve for the following reactions.

The **hydroxyl ion, $\bar{\mathbf{O}}\mathbf{H}$,** forms yellow cuprous hydroxid at first. At ordinary temperatures, this slowly dehydrates and precipitates red $\mathrm{Cu_2O}$. The reaction is hastened by boiling.

The **carbonate ion, $\bar{\bar{\mathbf{C}}}\mathbf{O}_3$,** produces the same precipitate. Since no cuprous salts of acids containing oxygen are known, the $\bar{\mathrm{O}}\mathrm{H}$ ion, produced by hydrolysis of the carbonate, is the active agent and precipitates $(\mathrm{CuOH})_2$.

The **sulfid ion, $\bar{\bar{\mathbf{S}}}$,** precipitates black $\mathrm{Cu_2S}$, insoluble in alkalies and in dilute acid with the exception of warm $\mathrm{HNO_3}$, which oxidizes it to $\mathrm{Cu(NO_3)_2}$ and separates free sulfur.

The **cyanid ion, $\bar{\mathbf{C}}\mathbf{N}$,** precipitates white $(\mathrm{CuCN})_2$, soluble in excess of alkaline cyanids, forming complex cyanids of the proportions indicated by the formulae $\mathrm{K_3(CuC_4N_4)}$ and $\mathrm{K(CuC_2N_2)}$. In fairly concentrated solutions, the ion $(\mathrm{Cu}\overset{\equiv}{\mathrm{C}}_4\mathrm{N}_4)$ is very stable, decomposing into the simple $(\overset{+}{\mathrm{Cu}})_2$ ion to such a small extent that the $\overset{=}{\mathrm{S}}$ ion gives no precipitate. In dilute solutions, this ion decomposes almost entirely into $(\mathrm{Cu}\overset{-}{\mathrm{C}}_2\mathrm{N}_2)$, which is much less stable, and the solution is precipitated by the $\overset{=}{\mathrm{S}}$ ion.

SILVER (Argentum). Ag. 107.9.

Silver is a brilliant white metal, under ordinary conditions not attacked by oxygen or other constituents of the atmosphere at any temperature. It unites readily with the halogens and with sulfur, with the latter element forming black $\mathrm{Ag_2S}$. Slight traces of $\mathrm{H_2S}$ in the air account for the tarnishing of silver according to the equation:

$$4\mathbf{Ag} + 2H_2S + O_2 \rightarrow 2\mathbf{Ag_2S} + 2\mathrm{H_2O}$$

Metallic silver is insoluble in HCl but readily dissolves in $\mathrm{HNO_3}$; also in hot concentrated $\mathrm{H_2SO_4}$ with the evolution of $\mathrm{SO_2}$. In the presence of oxygen, silver dissolves in solutions of the alkaline cyanids according to the reaction:

$$4\mathbf{Ag} + 8\mathrm{KCN} + O_2 + 2\mathrm{H_2O} \rightarrow 4\mathrm{K(AgC_2N_2)} + 4\mathrm{KOH}$$

Silver, like copper, shows a decided disinclination to pass into the ionic condition, as is indicated by the fact that considerable energy is absorbed when the metal becomes the ion. This partially accounts for the fact that silver does not dissolve readily in acids but requires also an oxidizing action to make it pass into the ionic form. Silver stands very near the bottom of the Potential Series. (See page 327.) If metallic zinc, iron, lead, tin, mercury, or almost any other metal with the exception of gold and platinum, be introduced into a solution containing the $\overset{+}{\mathrm{Ag}}$ ion, metallic silver is deposited while the other metal passes into the ionic condition and goes into solution. The following equation illustrates the reaction and shows the greater tendency of these metals to pass into the ionic condition.

$$\mathbf{Hg} + 2\overset{+}{\mathrm{Ag}} + 2\overset{-}{\mathrm{NO}}_3 \rightarrow \overset{++}{\mathrm{Hg}} + 2\mathbf{Ag} + 2\overset{-}{\mathrm{NO}}_3$$

On the other hand, silver passes with the greatest readiness from the ionic into the metallic condition and the metal may be obtained from its salts without difficulty by the action of heat and reducing agents.

Heated before the **blowpipe** with $\mathrm{Na_2CO_3}$ on charcoal, all the salts of silver are decomposed. A brilliant white metallic globule is formed, without coating on the charcoal (difference from Bi, Pb and Sn), which dissolves readily in HNO_3 (difference from Sn) and gives an immediate precipitate even in hot dilute solution when treated with HCl (difference from Pb and Bi).

The common **silver ion** is $\overset{+}{\mathbf{Ag}}$. In the presence of NH_3, complex silver-ammonia ions are formed, of which $\overset{+}{Ag}(NH_3)_2$ is the best known. In both of these forms silver acts as kathion. In other ions, the silver-cyanid, $Ag\overset{-}{C}_2N_2$, and a very complex silver-thiosulfate ion, probably $Ag_2(S_2\overset{=}{O}_3)_3$, the metal is a constituent of the anion.

Silver compounds are usually colorless and insoluble, the nitrate being the only common salt which is readily soluble. It dissolves in half its weight of water and crystallizes from solution without water of crystallization, a tendency exhibited by all silver salts. The fact that the salts of this metal do not hydrolyze is an indication that silver is a base-forming element of considerable strength. The nitrate, acetate and sulfate are fairly soluble, but may be precipitated from concentrated solutions. Compounds formed by the complex silver ions are generally soluble.

The **hydroxyl ion,** $\overset{-}{\mathbf{OH}}$, added to solutions containing the $\overset{+}{Ag}$ ion, causes the formation of AgOH, which, at ordinary temperatures, immediately loses water and forms Ag_2O, a brown-black precipitate, soluble in about 15,000 parts of water. Its solution has an alkaline reaction and therefore must contain $\overset{-}{OH}$ ions. Hence some AgOH must exist in solution. Measurements of its electrical conductivity seem to indicate that it is about one-third dissociated at this dilution. Consequently, it is a very much weaker base than the fixed alkalies and alkaline-earth hydroxids, but is stronger than ammonium hydroxid.

Silver oxid is entirely decomposed at 250° into oxygen and silver.

When precipitated by a solution of NaOH or KOH, silver oxid is not affected by an excess of the reagent. If NH_4OH is sparingly added to a solution containing $\overset{+}{Ag}$ ions, Ag_2O is precipitated, but dissolves in the slightest excess of the precipitant. Owing to the decomposition of the undissociated NH_4OH into H_2O and NH_3, a complex ion, $\overset{+}{Ag}(NH_3)_2$, is formed, the salts of which are soluble. Since this complex ion forms with great readiness and is decomposed but little into NH_3 and the simple silver ion, the presence of NH_3 decreases the concentration of the $\overset{+}{Ag}$ ion very decidedly (see page 36), hence the precipitated Ag_2O, and, similarly, most other salts of silver, dissolve readily in NH_4OH.

The silver-ammonia ion and, less readily, the simple $\overset{+}{Ag}$ ion, may be reduced with the greatest ease and metallic silver may be deposited by the action of carbonaceous matter, in general, and, especially, by tartaric and citric acids, aldehyde and the sugars. Inasmuch as part of the silver adheres closely to the glass vessel in which the reduction takes place and forms a brilliant mirror, this reaction is used as a test for certain of these substances. (See page 285.)

The stains which are caused by silver solutions coming in contact with organic matter are due to this same reducing action, the finely divided metallic silver being black in color. A solution of potassium cyanid, by dissolving the metal, will remove the stain.

The **carbonate ion, $\mathbf{\overline{CO}_3}$,** causes the precipitation of white $\mathrm{Ag_2CO_3}$, which soon undergoes partial decomposition into $\mathrm{CO_2}$ and $\mathrm{Ag_2O}$, the latter giving a yellow tinge to the precipitate. If $\mathrm{(NH_4)_2CO_3}$ is used as the precipitant, $\mathrm{Ag_2CO_3}$ dissolves somewhat in excess, since $\mathrm{(NH_4)_2CO_3}$ hydrolyzes considerably. Free $\mathrm{NH_3}$ is therefore present in the solution and causes the formation of the soluble silver-ammonia ion.

The **sulfid ion, $\mathbf{\overline{S}}$,** precipitates black $\mathrm{Ag_2S}$ from both acid and alkaline solutions. This compound dissolves when treated with $\mathrm{HNO_3}$ since it is oxidized to free sulfur (or $\mathrm{H_2SO_4}$) and $\mathrm{AgNO_3}$. Silver sulfid is an extremely insoluble substance, hence it does not dissolve appreciably even in the strong acids, nor in $\mathrm{NH_4OH}$ or dilute KCN.

The **sulfate ion, $\mathbf{\overline{SO}_4}$,** precipitates white $\mathrm{Ag_2SO_4}$ from neutral solutions only, since it is exceedingly soluble in traces of acid and of ammonia.

The **chromate ion, $\mathbf{\overline{CrO}_4}$,** precipitates red $\mathrm{Ag_2CrO_4}$, which, being the salt of an acid only moderately strong, is soluble in the strong acids. Like other silver salts which are appreciably soluble, it dissolves in $\mathrm{NH_4OH}$ with the formation of the silver-ammonia ion.

The **chlorid ion, $\mathbf{\overline{Cl}}$,** precipitates curdy white AgCl, soluble in about 700,000 parts of water, insoluble in all dilute acids. It dissolves with extreme readiness in $\mathrm{NH_4OH}$, also in KCN and $\mathrm{Na_2S_2O_3}$. In the presence of the cyanid ion, $\mathrm{\overline{CN}}$, the silver ion forms the complex silver-cyanid ion, $\mathrm{Ag\overline{(CN)}_2}$.

$$\overset{+}{\mathrm{Ag}} + 2\overline{\mathrm{CN}} \rightarrow \mathrm{Ag\overline{C}_2N_2}$$

Since $\mathrm{Ag\overline{C}_2N_2}$ is very stable and decomposes but little into the simple ions, the presence of the $\mathrm{\overline{CN}}$ ion reduces the concentration of $\overset{+}{\mathrm{Ag}}$ ions decidedly and, therefore, the AgCl dissolves readily. (See page 36.)

In sodium thiosulfate, AgCl dissolves forming a solution from which crystallizes a salt having the proportions represented by the formula $(Na_2S_2O_3)_2.\mathrm{Ag_2S_2O_3}$. The complex ion formed by this salt is very stable, but, when boiled with acids, decomposes with the formation of black Ag_2S.

In concentrated solutions of HCl and other chlorids, AgCl dissolves readily, probably forming complex compounds of the type $HAgCl_2$, which separate $\overset{+}{Ag}$ ions only on diluting, in which case AgCl is again precipitated.

The **bromid ion, $\overset{-}{Br}$,** precipitates white AgBr, soluble in about 1,000,000 parts of water, and very similar to AgCl. It dissolves in KCN and $Na_2S_2O_3$ as does AgCl and for similar reasons. It is less readily soluble in NH_4OH, however.

The **iodid ion, $\overset{-}{I}$,** precipitates pale yellow AgI which resembles the other halids of silver and is soluble in about 1,500,000 parts of water. Like them it dissolves readily in KCN and $Na_2S_2O_3$, but is not appreciably soluble in NH_4OH. The cause for this varying solubility of the silver halids in NH_4OH will be apparent from the following reasoning.

In a saturated solution of AgCl there will be concentration of $\overset{+}{Ag}$ ions which may be represented, let us say, by 100. Since AgBr is less soluble than AgCl, the concentration of $\overset{+}{Ag}$ ions in a saturated solution of the latter salt will be less, and may be represented by 75. Being less soluble than either, AgI will give a concentration which, on the same scale, may be taken as 50. The concentration of $\overset{+}{Ag}$ ions due to the decomposition of the very soluble-but-stable, complex silver-ammonia ion may be represented by 35. The same ion, $Ag(\overset{+}{N}H_3)_2$, is formed by dissolving AgCl, AgBr and AgI in NH_4OH. Therefore the final concentration of $\overset{+}{Ag}$ ions will be the same in each case. But the relative reduction in the case of the chlorid is much greater than with the bromid, therefore, AgCl is more soluble in NH_4OH than AgBr is. The reduction in the case of the iodid is relatively too small to cause appreciable solution. The fact that all three silver halids dissolve in KCN and $Na_2S_2O_3$ is due to a stability on the part of the silver-cyanid and silver-thiosulfate ions greater than that possessed by the silver-ammonia ion. Therefore the final concentration of $\overset{+}{Ag}$ ions is less in every case and the relative reduction is sufficiently great to cause solution.

On the addition of acids to a solution containing the silver-ammonia ion, a process, the reverse of that by which it is formed, takes place. The $\overset{+}{H}$ ions combine with NH_3 to form $\overset{+}{N}H_4$ ions, thus causing the complex ion to decompose and give rise to the simple $\overset{+}{Ag}$ ion. In this manner, the concentration of the $\overset{+}{Ag}$ ion is increased and AgCl, AgBr, or AgI is precipitated once more.

By exposure to light all of the silver halids turn dark and liberate a part of the halogen, forming probably a compound of a lower type such as Ag_2Cl. The original color of a darkened silver halid is restored by chlorin or bromin water.

All the silver halids may be decomposed by bringing them in contact with metallic zinc and covering them with H_2SO_4.. By the action of the nascent hydrogen formed by the interaction of the acid and the metal, metallic silver is thrown out and hydrogen-halogen acids formed.

The **cyanid ion, $\bar{C}N$,** precipitates white AgCN, insoluble in HNO_3, but readily soluble in NH_4OH, $Na_2S_2O_3$, and an excess of alkaline cyanid.

The **phosphate ion, $\overset{\equiv}{P}O_4$,** precipitates yellow Ag_3PO_4.

The **arsenate ion, $\overset{\equiv}{As}O_4$,** separates chocolate-colored Ag_3AsO_4.

The **arsenite ion, $\overset{\equiv}{As}O_3$,** causes yellow Ag_3AsO_3 to fall.

As would be expected, all of these salts are soluble in HNO_3 and NH_4OH as well, and can be precipitated only from neutral solutions.

Inasmuch as the $\overset{+}{Ag}$ ion is an important reagent in detecting and differentiating between acid radicles or anions, the following is a list of the salts formed by the $\overset{+}{Ag}$ ion with those acids which will be considered in the present scheme of analysis:

Acid.	*Salt.*	*Color.*	*H_2O.*	*HNO_3.*	*NH_4OH.*
Acetic	$Ag(C_2H_3O_2)$	White	Sol.*	Sol.	Sol.
Arsenic	Ag_3AsO_4	Chocolate	Insol.	Sol.	Sol.
Arsenious	Ag_3AsO_3	Yellow	Insol.	Sol.	Sol.
Boric	$AgBO_2$	White	Insol.	Sol.	Sol.
Carbonic	Ag_2CO_3	White	Insol.	Sol.	Sol.
Chloric	$AgClO_3$	White	Sol.	Sol.	Sol.
Chromic	Ag_2CrO_4	Red	Insol.	Sol.	Sol.
Cyanic	AgOCN	White	Insol.	Sol.	Sol.
Ferricyanic	$Ag_3(FeC_6N_6)$	Orange	Insol.	Sol.	Sol.
Ferrocyanic	$Ag_4(FeC_6N_6)$	White	Insol.	Sol.	Insol.
Hydrobromic	AgBr	White	Insol.	Insol.	Sol.
Hydrochloric	AgCl	White	Insol.	Insol.	Sol.
Hydrocyanic	AgCN	White	Insol.	Insol.	Sol.
Hydrofluoric	AgF	White	Sol.	Sol.	Sol.
Hydriodic	AgI	Yellow	Insol.	Insol.	Insol.
Hydrosilicofluoric	Ag_2SiF_6	White	Sol.	Sol.	Sol.
Hydrosulfuric	Ag_2S	Black	Insol.	Sol.	Insol.
Hypochlorous	AgOCl (unstable)	——	——	——	——
Nitric	$AgNO_3$	White	Sol.	Sol.	Sol.
Nitrous	$AgNO_2$	White	Sol.*	Sol.	Sol.
Oxalic	$Ag_2C_2O_4$	White	Insol.	Sol.	Sol.
Perchloric	$AgClO_4$	White	Sol.	Sol.	Sol.
Permanganic	$AgMnO_4$	Purple	Sol.	Sol.	Sol.
Phosphoric	Ag_3PO_4	Yellow	Insol.	Sol.	Sol.
Silicic	—— (unknown)	——	——	——	——
Sulfuric	Ag_2SO_4	White	Sol.*	Sol.	Sol.
Sulfurous	Ag_2SO_3	White	Insol.	Sol.	Sol.
Thiocyanic	AgSCN	White	Insol.	Insol.	Sol.
Thiosulfuric	$Ag_2S_2O_3$	White	Insol.	Sol.	Sol.
Tartaric	$Ag_2(C_4H_4O_6)$	White	Insol.	Sol.	Sol.

* *May be precipitated* from fairly concentrated solutions.

GOLD (Aurum). Au — 197.2.

Gold is a soft, malleable, heavy, yellow metal. It is not acted upon by the constituents of the atmosphere at any temperature and, with silver, platinum and a few other elements, is known as a "noble metal."

Gold does not dissolve in any acid but, since it is attacked by the halogens at ordinary temperatures, it dissolves readily in aqua regia because of the free chlorin which this reagent contains. Like the other "noble metals," gold shows a very strong disinclination to pass into the ionic condition and energy is absorbed when the metal takes on the electric charge. Gold stands at the very bottom of the Potential Series, hence if any other metal is introduced into a solution containing salts of gold, the latter metal is deposited and the former goes into solution.

All **gold salts** are unstable and are readily reduced to the metallic condition by heat and by reducing agents of all kinds. Ferrous and stannous salts, oxalic and sulfurous acids all effect the reduction to the metal in acid solutions at ordinary temperatures. When stannous chlorid is used as a reducing agent, the finely divided gold is of a red or purple color and under the name of "purple of Cassius" affords a well-known test for this metal.

Heated before the **blowpipe** on charcoal with Na_2CO_3, all gold salts leave a yellow globule of the metal, insoluble in nitric acid.

With oxygen, metallic gold does not unite directly, nevertheless by indirect means two oxids may be obtained, a dark violet monoxid, Au_2O, and a brown trioxid, Au_2O_3. Each of these substances may be considered as the basis from which a series of gold salts is derived.

The **univalent aurous salts** are nearly colorless, generally insoluble and are decomposed slowly by water according to the equation:

$$3\mathrm{AuCl} \rightarrow \mathrm{AuCl_3} + \mathbf{2Au}$$

For these reasons the aurous ion, $\overset{+}{\mathrm{Au}}$, is but little known.

Aurous cyanid, AuCN, unites with potassium cyanid to form a compound, $KAuC_2N_2$, in which the gold is a constituent of the anion, $\mathrm{Au}\overset{-}{\mathrm{C}}_2\mathrm{N}_2$. This compound is fairly stable and is of importance in the metallurgy of gold, for, in the presence of air, metallic gold dissolves in potassium cyanid solutions according to the equation:

$$\mathbf{4Au} + 8\mathrm{KCN} + O_2 + \mathrm{H_2O} \rightarrow 4\mathrm{KAuC_2N_2} + 4\mathrm{KOH}$$

Auric salts are trivalent and somewhat more stable than aurous salts. They are generally light yellow in color, usually soluble and in solution give rise to the auric ion, $\overset{+++}{\mathrm{Au}}$.

Gold salts of acids containing oxygen are but little known since they are very unstable and decompose readily even in solution.

Auric chlorid, $AuCl_3$, is the most important gold salt. It is a light-yellow, deliquescent substance which at 180° breaks down into aurous chlorid and free halogen and, at a somewhat higher temperature, is entirely decomposed into its elements. In solution, it gives rise to the auric ion, $\overset{+++}{Au}$. Auric chlorid readily unites with hydrochloric acid to form a crystalline compound, hydrochlorauric acid, $HAuCl_4$, in which the gold acts as a constituent of the anion, $Au\overline{Cl}_4$. Several salts of this acid are known. Of these the sodium compound, $NaAuCl_4$, finds use in photography as a "toning solution."

The **hydroxyl ion, $\overline{O}H$,** added to a solution containing the auric ion, $\overset{+++}{Au}$, causes a red, flocculent precipitate which seems almost identical in appearance with ferric hydroxid. Like aluminum, zinc, lead and tin and certain other hydroxids, auric hydroxid acts either as an acid or as a base. It is readily soluble in acids, forming salts in which gold plays the part of a metal. It dissolves in alkalies as well, giving rise to compounds of the composition $KAuO_2$. These salts are known as aurates, for in them gold acts as an acid-forming element. So readily does auric hydroxid dissolve in an excess of sodium or potassium hydroxid that, in dilute gold solutions, no precipitate is ordinarily obtained.

Ammonium hydroxid, in distinction from sodium and potassium hydroxids, precipitates from solutions containing the $\overset{+++}{Au}$ ion, a flocculent, brown powder which, when dry, is explosive. It has the composition, $AuN_2H_3.3H_2O$, and is known as "fulminating gold."

The **carbonate ion, $C\overline{O}_3$,** from solutions of alkaline carbonates, because of hydrolysis acts as does the hydroxid ion.

The **sulfid ion, $\overline{S}$,** precipitates a black substance, the composition of which varies from Au_2S_3 to Au_2S or, apparently, it may contain metallic gold. The substance is insoluble in acids, but dissolves in aqua regia and in solutions of alkaline sulfids, forming in the latter case a thioaurate analogous to thioantimonates and similar compounds. This fact causes gold to be separated in qualitative analysis along with antimony and arsenic in the tin group.

Group 2, First Type.

Beryllium 9.1; **Magnesium 24.4; Calcium 40.1; Strontium 87.6; Barium 137.4;** Radium 225.

The alkaline earths, as this group is called, are soft, light, lustrous metals. Although they are unstable in the air and decompose water, the action is not so vigorous as with the alkali metals. The chemical activity of the elements increases as the atomic weight rises, but all these substances are reactive, forming stable compounds from which the elements may be obtained only with difficulty. The members of this group always show a valence of two. The oxids unite readily with water to form hydroxids which act as moderately strong bases, barium hydroxid dissociating somewhat more than magnesium hydroxid. Salts of this group are generally colorless. The solubility of the hydroxids increases, and of the sulfates decreases, as the atomic weight rises. With the exception of magnesium, salts of the common metals give color to a Bunsen flame.

Beryllium, and radium especially, are very rare elements, and they will not be considered in detail.

MAGNESIUM. Mg — 24.4.

Magnesium is a light, silver-white, crystalline metal. At ordinary temperatures it tarnishes somewhat in the atmosphere, forming a compact film of the oxid which acts as a protective coating. Heated in the air, it burns with an intense white light to the oxid. Because of the great actinic power of this light, it is much used in photography for "flash lights." The metal is capable of taking nitrogen as well as oxygen from the air, forming the nitrid, Mg_3N_2.

The **metal** passes readily into the ionic condition and, therefore, dissolves in all acids. Even the concentration of $\overset{+}{H}$ ions due to the dissociation of water is sufficient at 100° to liberate hydrogen and form $Mg(OH)_2$. This substance, being insoluble, soon coats over the metal and prevents further action. If ammonium salts be present in solution to dissolve the hydroxid (see later), the action proceeds freely. Magnesium is not precipitated from solutions of its salts by other metals, but, on the contrary, with the exception of aluminum and chromium, under proper conditions magnesium will precipitate all the common metals from solutions of their salts, provided the metals do not react with water. When magnesium passes into the ionic condition, more energy is liberated than in the case of any other metal with the exception of the alkali and alkaline-earth metals. For this reason its salts are reduced in the "dry way" only and with considerable difficulty.

Magnesium oxid, MgO, is called "magnesia," and like oxids generally it may be formed by burning the metal or by heating the hydroxid, carbonate, nitrate or salts of organic acids (which break down first into carbonates). It fuses only at the highest obtainable temperatures. It is a light white substance, but slightly soluble in water, reacting with it to form the hydroxid.

Magnesium salts are generally colorless and usually soluble. Of the common salts, only the hydroxid, carbonate and phosphate are insoluble. Magnesium salts contain the metal in the bivalent condition, acting as a base-forming element distinctly stronger than the ordinary metals, yet not sufficiently strong to protect its compounds from hydrolysis. They give no color to a Bunsen flame.

The simple **magnesium ion** is $\mathbf{\overset{++}{Mg}}$. Some complex ions are known.

For the reactions of the $\overset{++}{Mg}$ ion, any soluble simple salt will serve. The nitrate, $Mg(NO_3)_2.6H_2O$, is deliquescent and soluble in half its weight of water. The acetate, $Mg(C_2H_3O_2)_2.4H_2O$, is also deliquescent and extremely soluble.

The **hydroxyl ion, $\mathbf{\overset{-}{OH}}$**, precipitates white, gelatinous $Mg(OH)_2$, soluble in about 100,000 parts of pure water, but the presence of small amounts of impurities generally increases its solubility greatly. It dissociates to nearly the same extent as the other hydroxids of this group at the same dilution, but, owing to its insolubility, affects litmus slowly.

If NH_4OH be used as the reagent for introducing the $\overset{-}{OH}$ ion, only a partial precipitation of the magnesium as hydroxid is effected. This phenomenon is due partly to the reduced concentration of $\overset{-}{OH}$ ions caused by the repression of the ionization of the weak base, NH_4OH, by its more readily-dissociating salts (see page 31), and partly owing to the formation of soluble, complex magnesium-ammonium salts of the type $(NH_4)_2MgCl_4$. These compounds do not separate the simple $\overset{++}{Mg}$ ion at ordinary dilutions to any great extent, but they dissociate into $(\overset{+}{NH_4})$ and $M\overset{=}{g}Cl_4$ ions. In the presence of sufficient NH_4Cl (or other ammonium salt), no precipitation of $Mg(OH)_2$ will take place. A solution of this character (usually 1 gram-molecule of $MgCl_2$ plus 2 of NH_4Cl rendered strongly alkaline with NH_4OH) is known as "magnesia mixture" and is used as a precipitant for phosphoric and arsenic acids. This same property of forming double salts with ammonium compounds is possessed by cobalt, nickel, manganese zinc and ferrous iron as well.

The **carbonate ion, $\mathbf{\overset{=}{CO}_3}$**, causes a white precipitate, consisting of a mixture of $MgCO_3$ and $Mg(OH)_2$, owing to hydrolysis. If $(NH_4)_2CO_3$ be used as the precipitant, only a partial precipitation ensues, owing to the formation of the complex salt already mentioned. In the presence of ammonium salts, no precipitate will fall.

The precipitate obtained with alkaline carbonates dissolves in water containing carbon dioxid (*i. e.*, carbonic acid), forming a soluble acid carbonate similar in all respects to the corresponding salt of calcium. (See page 95.) By slow evaporation of such a solution, the normal carbonate, $MgCO_3$, which is the mineral magnesite, crystallizes. Like calcium salts, magnesium salts in solution make water "hard."

The **sulfid ion, $\overset{=}{\mathbf{S}}$,** causes no precipitate, for MgS is formed only in the "dry way" and in aqueous solution is hydrolyzed into $Mg(OH)_2$ and H_2S. Since $Mg(OH)_2$ is insoluble and is thus removed from the sphere of action, complete hydrolysis takes place, the reaction proceeding practically only in the direction indicated by the equation:

$$MgS + 2HOH \rightarrow \mathbf{Mg(OH)_2} + H_2S$$

If $(NH_4)_2S$ is used to introduce the $\overset{=}{S}$ ion, a partial precipitation of $Mg(OH)_2$ may be obtained if no other ammonium salts are present. With H_2S, however, no $Mg(OH)_2$ is precipitated because of the acid formed during the metathesis indicated by the equation:

$$MgCl_2 + H_2S \rightarrow MgS + 2HCl$$

The **sulfate ion, $\mathbf{S\overset{=}{O}_4}$,** causes no precipitation since $MgSO_4.7H_2O$ is soluble in less than three parts of H_2O, crystallizing from solutions in the form characteristic of the "vitriols." (See page 188.) It is the only common salt of magnesium that does not deliquesce. Under the name of "Epsom salt," it finds medicinal use.

The **chromate ion, $\mathbf{Cr\overset{=}{O}_4}$,** causes no precipitate, as $MgCrO_4$ is very soluble.

The **chlorid ion, $\overset{-}{\mathbf{Cl}}$,** causes no precipitate, for $MgCl_2.6H_2O$, like the bromid, iodid and cyanid, is extremely soluble, dissolving in half its weight of water. In solution, it hydrolyzes considerably and, on evaporation, the volatile HCl escapes, leaving behind an oxychlorid, Mg_2OCl_2. For this reason chiefly, sea-water can not be used in boilers as the acid corrodes the metal.

The **fluorid ion, $\overset{-}{\mathbf{F}}$,** precipitates white MgF_2 which is only slowly soluble in the stronger acids.

The **phosphate ion, $\mathbf{P\overset{\equiv}{O}_4}$,** precipitates white $Mg_3(PO_4)_2$ which is soluble in about 5000 parts of H_2O. If HNa_2PO_4 is used as the precipitating reagent, tertiary magnesium phosphate does not fall, but rather the secondary or acid magnesium phosphate, $HMgPO_4$, which is soluble in less than 500 parts of H_2O. In the presence of NH_4OH, however, $(NH_4)MgPO_4.6H_2O$ is precipitated which, on boiling, assumes a crystalline form. This salt is soluble in about 10,000 parts of H_2O, but, in the presence of considerable NH_4OH, requires more than 50,000 parts for solution.

The **oxalate ion, $\overset{=}{C_2O_4}$**, may precipitate from solutions containing the $\overset{++}{Mg}$ ion white magnesium oxalate, $MgC_2O_4.2H_2O$, which requires 1500 parts of H_2O for solution. An excess of any alkaline oxalate, however, forms double oxalate salts of several different proportions, all of which are soluble.

CALCIUM. Ca — 40.1.

Calcium is a silvery-white, crystalline, malleable metal. In dry air it is stable but, under ordinary conditions, it is quickly attacked, forming $CaCO_3$ and liberating hydrogen. It has no industrial uses and is merely of scientific interest.

The **metal** dissolves very readily, even in dilute solutions of acids as weak as H_2CO_3, forming salts in which the element is always divalent. The concentration of $\overset{+}{H}$ ions, given by pure H_2O, is sufficient to cause the metal to dissolve slowly at ordinary temperatures, liberating hydrogen and forming the hydroxid according to the reaction:

$$\mathbf{Ca} + 2\overset{+}{H} + 2\overset{-}{OH} \rightarrow \overset{++}{Ca} + 2\overset{-}{OH} + H_2$$

When the element passes into the ionic condition a large amount of energy is liberated, hence its salts are extremely stable. The metal acts as a base-forming element of considerable strength, consequently salts of the strong acids show no hydrolysis. With few exceptions calcium salts are colorless.

Calcium salts color a Bunsen flame orange. This indication is somewhat masked by the presence of other members of this group. If the salt which is heated be moistened with HCl, the calcium flame will flash out for a moment at the start, since $CaCl_2$ requires less heat to volatilize and decompose it than either $BaCl_2$ or $SrCl_2$. Barium and strontium will appear after the calcium is gone and the indication of these elements will be more lasting.

With the **spectroscope**, calcium is detected chiefly by a green and an orange line about equally distant from the ever-present sodium line. (See frontispiece.)

The only **calcium ion** definitely known is $\overset{++}{\mathbf{Ca}}$. For the reactions of this ion any soluble calcium salt will serve. The nitrate, $Ca(NO_3)_2.4H_2O$ is deliquescent and soluble in about one-quarter of its weight of water. The anhydrous salt is readily soluble in amyl alcohol and by this means may be separated from barium and strontium, which are insoluble in the same solvent. (See page 270.)

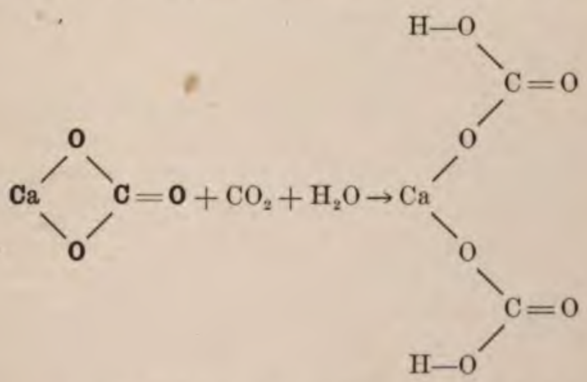
The acetate, $Ca(C_2H_3O_2)_2.5H_2O$, is efflorescent.

The **hydroxyl ion, $\mathbf{O\bar{H}}$,** produces no precipitate under ordinary conditions, for $Ca(OH)_2$ is soluble in about 800 parts of cold water. It requires more than 1600 parts at 100°, for its solubility decreases as the temperature rises. Concentrated solutions of NaOH or KOH may produce a precipitate but the $\bar{O}H$ ion is never present in NH_4OH solutions in concentration sufficient to do so.

Calcium hydroxid is a strong base, its dissociation being surpassed in a marked degree only by the hydroxids of the alkali metals. As it is by far the cheapest reagent of this kind, it is used for all industrial purposes where a strong base is required. It is obtained by "burning limestone," *i. e.*, heating the carbonate, $CaCO_3$, which loses CO_2 and forms the oxid, CaO, which is lime. Treated with water, lime "slacks" and forms the hydroxid or slacked lime. Like all strong bases, calcium hydroxid absorbs CO_2 from the atmosphere, thus reforming the carbonate. A solution of $Ca(OH)_2$ is known as "lime-water."

The **carbonate ion, $\mathbf{\bar{C}O_3}$,** precipitates white, amorphous $CaCO_3$ which, on warming, readily passes into the crystalline condition, which is the mineral calcite. During this change, liquids containing $CaCO_3$ in suspension become much less opaque since the crystalline form is much more dense and compact. On standing, it settles rapidly. At a bright red heat, *i. e.*, about 800°, $CaCO_3$ breaks down readily into CO_2 and CaO.

Calcium carbonate is soluble in about 60,000 parts of H_2O. It is much more readily soluble in water containing CO_2, forming acid calcium carbonate, which dissolves in about 1000 parts of H_2O.



On heating, all acid carbonates are decomposed into normal carbonates, water and CO_2, thus reversing the reaction. Lime salts, together with magnesium salts, present in solution make water "hard," i. e., form insoluble compounds with soap, thus preventing its cleansing action. When these elements are present as acid carbonates, water is said to be "temporarily hard," for, on boiling, normal carbonates are precipitated and the "hardness" removed. On exposing a solution of acid calcium carbonate to the air, the same reaction takes place slowly as the excess of CO_2 escapes. In this way $CaCO_3$ is deposited as stalagmites and stalactites in caves.

In the presence of NH_4Cl, $CaCO_3$ dissolves, on boiling, owing to the metathesis—

$$\mathbf{CaCO_3} + 2NH_4Cl \rightarrow CaCl_2 + (NH_4)_2CO_3$$

When heated, $(NH_4)_2CO_3$ decomposes into NH_3, CO_2 and H_2O, which are removed from solution by boiling, thus causing the reaction to proceed in the direction indicated. For this reason, in the presence of considerable NH_4Cl, a small amount of $(NH_4)_2CO_3$ may not precipitate calcium and the other members of this group as carbonates completely, especially if the solution is hot, as is usually necessary.

The **sulfid ion, $\overline{\overline{S}}$,** under ordinary conditions produces no precipitate for CaS, though somewhat insoluble, is hydrolyzed, forming soluble products, first CaSH and finally $Ca(OH)_2$ and H_2S.

The **sulfate ion, $S\overline{\overline{O}}_4$,** causes a white precipitate of $CaSO_4.2H_2O$ in solutions of fair concentration only, since the precipitate is soluble in about 500 parts of water. If $CaSO_4$ in solution be used as the precipitating reagent, obviously no precipitate will form (distinction from Ba and Sr).

$$CaCl_2 + CaSO_4 \rightarrow CaSO_4 + CaCl_2$$

The naturally-occurring sulfate, gypsum, is heated until it has lost most of its water of crystallization. The dehydrated product is known as "plaster of Paris" and, on treatment with water, takes up its water of crystallization once more and "sets" to a compact mass of crystals.

Calcium or magnesium present in solution as sulfates cannot be removed by boiling. Water containing these elements as sulfates is said to be "permanently hard," since it cannot be "softened" except by addition of chemical reagents.

Since $CaSO_4$ is so much more soluble than $CaCO_3$, on boiling with Na_2CO_3, the former is readily transposed into the latter.

$$\mathbf{CaSO_4} + Na_2CO_3 \rightarrow \mathbf{CaCO_3} + Na_2SO_4$$

The **chromate ion, $Cr\overline{\overline{O}}_4$,** produces no precipitate except in concentrated solutions, for $CaCrO_4$ is soluble in about 200 parts of H_2O. Solutions of alkaline dichromates never contain sufficient concentration of $\mathrm{C}\overset{=}{\mathrm{r}}\mathrm{O}_4$ ions to cause a precipitate.

The **chlorid ion, $\bar{\mathbf{C}}\mathbf{l}$,** produces no precipitate, for the chlorid, $CaCl_2$, like the bromid and iodid, is deliquescent and very soluble. The anhydrous salt dissolves in about 1½ parts of H_2O.

The **fluorid ion, $\bar{\mathbf{F}}$,** precipitates white CaF_2, soluble in about 27,000 parts of water. It is slowly soluble in HCl and other strong acids, for HF is a weak acid (see page 16). It occurs in nature as fluorspar or fluorite.

The **cyanid ion, $\bar{\mathbf{C}}\mathbf{N}$,** causes no precipitate, since $Ca(CN)_2$ is readily soluble.

The **phosphate ion, $\mathbf{P}\overset{\equiv}{\mathbf{O}}_4$,** precipitates white $Ca_3(PO_4)_2$, soluble in about 40,000 parts of H_2O, readily soluble even in acetic acid. By acid sodium phosphate, HNa_2PO_4, which is the ordinary precipitating reagent, $Ca_3(PO_4)_2$ is precipitated only in ammoniacal solutions. In neutral solutions, acid phosphate, $HCaPO_4$, falls. Diacid calcium phosphate, $CaH_4(PO_4)_2$, is the "soluble phosphate" present in fertilizers.

The **oxalate ion, $\mathbf{C}_2\overset{=}{\mathbf{O}}_4$,** precipitates white $CaC_2O_4.2H_2O$, soluble in about 140,000 parts of H_2O. Since oxalic acid, $H_2C_2O_4$, dissociates to a greater degree than $H(C_2H_3O_2)$, calcium oxalate is insoluble in acetic acid, although its precipitation may be held up somewhat if the concentration of acetic acid becomes too great. Calcium oxalate is readily soluble in the strong mineral acids, however. When precipitated from a cold solution the crystals of calcium oxalate are so minute as to run through a filter paper readily and produce a milky filtrate. By heating the liquid, either previous to or after precipitation, larger crystals are formed which may be filtered without difficulty.

STRONTIUM. Sr — 87.6.

Strontium so closely resembles calcium in all essential features that a detailed description is unnecessary. Its nature as an element and the properties of its compounds are usually intermediate between calcium on the one side and barium on the other.

Strontium salts color a Bunsen flame an intense crimson. As the chlorid is more volatile and easily decomposed than other salts, the best results are obtained by moistening the substance with HCl before heating.

With the **spectroscope,** strontium is detected by the presence of six bright red bands, one orange and one blue band. (See frontispiece.)

The only **strontium ion** is $\overset{++}{\mathbf{Sr}}$. For reactions of this ion, solutions of any soluble salt will serve. The nitrate, $Sr(NO_3)_2.4H_2O$, is efflorescent. The anhydrous salt is soluble in 5 parts of H_2O but is insoluble in boiling amyl alcohol (distinction from Ca).

The **hydroxyl ion, $\mathbf{O\overline{H}}$,** produces no precipitate except in very concentrated solutions, for $Sr(OH)_2.8H_2O$ is soluble in about 60 parts of H_2O.

The **carbonate ion, $\mathbf{\overline{CO}_3}$,** precipitates white $SrCO_3$, soluble in about 100,000 parts of H_2O. It is similar in all respects to $CaCO_3$ but requires a higher temperature to decompose it into CO_2 and SrO.

The **sulfate ion, $\mathbf{\overline{SO}_4}$,** precipitates white $SrSO_4$, soluble in about 10,000 parts of H_2O. Since $CaSO_4$ is much more soluble than $SrSO_4$, the introduction of a saturated solution of $CaSO_4$ into solutions containing the $\overset{++}{\text{Sr}}$ ion causes a precipitate which appears somewhat tardily, inasmuch as $SrSO_4$ does not separate from supersaturated solutions at once. This reaction serves to distinguish barium and calcium from strontium, for the former gives an immediate precipitate and the latter none at all.

Since $SrSO_4$ is more soluble than $SrCO_3$, on boiling with Na_2CO_3, the former is transposed into the latter compound.

The **chromate ion, $\mathbf{Cr\overline{O}_4}$,** precipitates, from concentrated solutions only, yellow $SrCrO_4$, soluble in about 800 parts of H_2O. Alkaline dichromate solutions contain the $\text{C}\overline{\text{r}}\text{O}_4$ ion in sufficient concentration to cause a precipitate in very concentrated solutions of strontium salts.

The **oxalate ion, $\mathbf{C_2\overline{O}_4}$,** precipitates white SrC_2O_4, fairly insoluble in water but somewhat soluble in acetic acid.

BARIUM. Ba — 137.4.

The **metal barium** closely resembles calcium in properties. It decomposes water readily at ordinary temperatures, forming $Ba(OH)_2$ and liberating hydrogen.

Barium salts, with few exceptions, are colorless. In all of its compounds the metal is bivalent.

Barium salts color a Bunsen flame green. Moistening the substance to be tested with HCl aids this reaction considerably, owing to the formation of $BaCl_2$ which is more volatile than other barium salts. Barium sulfate is not appreciably volatile at the temperature of the blowpipe and is not decomposed by HCl, therefore gives but little flame coloration. Heated on a platinum wire in the reducing flame it is converted to the sulfid which, on treatment with HCl, gives a satisfactory indication when reheated.

With the **spectroscope,** barium is indicated by a number of bright green lines. (See frontispiece.)

The only **barium ion** known is $\overset{++}{\mathbf{Ba}}$. For the reactions of this ion, any soluble salt will serve. The nitrate, $Ba(NO_3)_2$, crystallizes anhydrous from solution. It is soluble in about 11 parts of H_2O but is entirely insoluble in boiling amyl alcohol (like Sr, but unlike Ca). The acetate $Ba(C_2H_3O_2)_2$, is readily soluble.

The **hydroxyl ion,** $\overset{-}{\mathbf{OH}}$, produces no precipitate, for $Ba(OH)_2.8H_2O$ is soluble in about 20 parts of cold water and in about twice its own weight of boiling water. Barium hydroxid is a trifle more dissociated than $Ca(OH)_2$ at corresponding dilutions and its solution is known as "baryta water."

The **carbonate ion,** $\overset{=}{\mathbf{CO}}_3$, precipitates white, amorphous $BaCO_3$ which, on heating, becomes crystalline. It is soluble in about 50,000 parts of H_2O. In the presence of CO_2, the acid carbonate is formed, soluble in about 1000 parts of H_2O. On boiling with NH_4Cl, the carbonate dissolves and the chlorid is slowly formed, just as with $CaCO_3$. (See page 96.) It is found in nature as the mineral witherite.

Barium carbonate requires a much higher temperature—about 1500°—to decompose it into CO_2 and the oxid than does $CaCO_3$, being more stable under the influence of heat than any other carbonates except those of the fixed alkalies. Barium oxid, BaO, like CaO, unites with water forming the hydroxid which readily absorbs CO_2 and passes into carbonate again.

On heating in a current of air, BaO absorbs oxygen and becomes BaO_2. At a higher temperature it breaks down again into the monoxid and liberates oxygen.

Barium peroxid, treated with dilute acids, forms hydrogen peroxid, H_2O_2.

The **sulfid ion,** $\overset{=}{\mathbf{S}}$, causes no precipitate, for BaS is fairly soluble and hydrolyzes to soluble products as does CaS.

The **sulfate ion,** $\overset{=}{\mathbf{SO}}_4$, precipitates white $BaSO_4$, soluble in about 400,000 parts of water. The naturally-occurring product is the mineral baryte. It dissolves in concentrated H_2SO_4 somewhat, forming the acid sulfate, $BaH_2(SO_4)_2$, but is reprecipitated on diluting. Hydrochloric acid has no appreciable solvent effect. Since $BaSO_4$ is so much more insoluble than $BaCO_3$, on boiling $BaSO_4$ with Na_2CO_3, an appreciable reaction takes place only when the concentration of Na_2CO_3 approximates that of a saturated solution. Even then the metathesis can be completed only on filtering off the precipitate and treating with fresh Na_2CO_3 repeatedly, a method which is obviously not satisfactory. By fusion with

4–5 times its bulk of Na_2CO_3, $BaSO_4$ may be more readily transposed, however.

If a saturated solution of $CaSO_4$ be used to introduce the $S\overline{O}_4$ ion into solutions containing the $\overset{++}{Ba}$ ion, an immediate precipitate results (distinction from Sr and Ca).

The **chromate ion, $\mathbf{C\overline{r}O_4}$**, precipitates canary-colored $BaCrO_4$, soluble in about 250,000 parts of H_2O. It is not appreciably soluble in acetic acid, but dissolves readily in the strong acids. Solutions of alkaline dichromates contain $C\overline{r}O_4$ ions in sufficient concentration to cause a precipitate of $BaCrO_4$.

The **chlorid ion, $\mathbf{\overline{C}l}$**, produces no precipitate, for $BaCl_2.2H_2O$, like the bromid and iodid, is very soluble, requiring only 2 parts of water for its solution. In concentrated HCl, it is insoluble and if sufficient HCl be added to a solution containing $\overset{++}{Ba}$ ions, a precipitate will fall.

The **fluorid ion, $\mathbf{\overline{F}}$**, precipitates white BaF_2, which is somewhat more soluble in water than CaF_2.

The **phosphate ion, $\mathbf{P\overline{O}_4}$**, precipitates white $Ba_3(PO_4)_2$, soluble even in acetic acid. By acid sodium phosphate, HNa_2PO_4, the ordinary precipitating reagent for phosphates, $Ba_3(PO_4)_2$ is precipitated only in alkaline solutions. In neutral solutions $HBaPO_4$ falls.

The **oxalate ion, $\mathbf{C_2\overline{O}_4}$**, precipitates white BaC_2O_4, soluble in about 2500 parts of water. In the strong acids, as well as in hot acetic acid, it is readily soluble.

The **silicofluorid ion, $\mathbf{S\overline{i}F_6}$**, precipitates white $BaSiF_6$, soluble in about 3500 parts of H_2O at ordinary temperatures. In dilute HCl it is considerably more soluble, however, and from acid solutions requires some standing to effect appreciable precipitation.

Inasmuch as the $\overset{++}{Ba}$ ion is an important reagent in detecting and differentiating between acid radicles or anions, a list of salts formed by the $\overset{++}{Ba}$ ion with the acids considered in the present scheme of analysis is appended, together with the solubilities of each in water and dilute HCl. (See next page.)

Group 2, Second Type.

Zinc 65.4; Cadmium 112.4; Mercury 200.

The members of this group are heavy metals, each possessing a bright metallic luster. They do not pass as readily into the ionic condition as the first type metals do; the compounds are less stable and from them the elements may be obtained without difficulty. Their oxids unite with *water* only indirectly to form hydroxids, which are by no means as

Acid.	*Formula.*	*Color.*	*H_2O.*	*HCl.*
Acetic	$Ba(C_2H_3O_2)_2$	White	Sol.	Sol.
Arsenic	$Ba_3(AsO_4)_2$	White	Insol.	Sol.
Arsenious	$Ba(AsO_2)_2$	White	Insol.	Sol.
Boric	$Ba(BO_2)_2$	White	Insol.	Sol.
Carbonic	$BaCO_3$	White	Insol.	Sol.
Chloric	$Ba(ClO_3)_2$	White	Sol.	Sol.
Chromic	$BaCrO_4$	Yellow	Insol.	Sol.
Cyanic	$Ba(OCN)_2$	White	Sol.	Sol.
Ferricyanic	$Ba_3(FeC_6N_6)_2$	Red	Sol.	Sol.
Ferrocyanic	$Ba_2(FeC_6N_6)$	Yellow	Sol.	Sol.
Hydrobromic	$BaBr_2$	White	Sol.	Sol.
Hydrochloric	$BaCl_2$	White	Sol.	Sol.
Hydrocyanic	$Ba(CN)_2$	White	Sol.	Sol.
Hydrofluoric	BaF_2	White	Insol.	Sol.
Hydriodic	BaI_2	White	Sol.	Sol.
Hydrosilicofluoric	$BaSiF_6$	White	Insol.	Insol.
Hydrosulfuric	BaS	Lemon	Sol.	Sol.
Hypochlorous	$Ba(ClO)_2$	White	Sol.	Sol.
Nitric	$Ba(NO_3)_2$	White	Sol.	Sol.
Nitrous	$Ba(NO_2)_2$	White	Sol.	Sol.
Oxalic	BaC_2O_4	White	Insol.	Sol.
Perchloric	$Ba(ClO_4)_2$	White	Sol.	Sol.
Permanganic	$Ba(MnO_4)_2$	Purple	Sol.	Sol.
Phosphoric	$Ba_3(PO_4)_2$	White	Insol.	Sol.
Silicic	$BaSiO_3$	White	Insol.	Insol.
Sulfuric	$BaSO_4$	White	Insol.	Insol.
Sulfurous	$BaSO_3$	White	Insol.	Sol.
Thiocyanic	$Ba(SCN)_2$	White	Sol.	Sol.
Thiosulfuric	BaS_2O_3	White	Sol.	Sol.
Tartaric	$Ba(C_4H_4O_6)$	White	Insol.	Sol.

strong as those of the first type. They act as weak bases. As the atomic weight rises, the metals become more resistant to the atmosphere, more readily reduced from their compounds and their salts tend to become colored. The group is generally bivalent. Mercury forms a whole series of compounds which are usually considered univalent, however, and cadmium exhibits some slight tendency in the same direction.

ZINC. Zn — 65.4.

Zinc is a heavy, bluish-white, crystalline metal. It tarnishes but little in the atmosphere, owing to the formation of a compact film of the oxid, which prevents further action. When highly heated, it burns with a bluish-white flame. Commercial zinc, often called "spelter," contains small amounts of carbon, iron and copper. "Zinc dust," the finely divided metal obtained by cooling the vapor, always contains ZnO.

Pure zinc dissolves but slowly in HCl or H_2SO_4. The commercial article is readily soluble in acids, however, even in acetic acid, owing to the fact that the impurities form with the metal small electrolytic couples which hasten the solution of the positive plate (*i. e.*, the zinc) and liberate hydrogen abundantly. A considerable amount of energy is liberated during the passage into the ionic condition. Consequently, to obtain the metal from its compounds requires the expediture of a large amount of energy which is absorbed during the reaction. For this reason, zinc salts are readily reduced only in the "dry way" on heating. Zinc is not precipitated from solutions of its salts by any of the common metals,* but, on the contrary, causes most other metals to be precipitated from solutions of their salts.

Zinc, like aluminum (see page 115), is attacked by the strong alkalies, forming zincates according to the reaction:

$$\mathbf{Zn} + 2\mathrm{NaOH} \rightarrow \mathrm{Na_2ZnO_2} + H_2$$

or, writing the ionic equation:

$$\mathbf{Zn} + 2\ \overset{-}{\mathrm{OH}} \rightarrow \overset{=}{\mathrm{ZnO}}_2 + H_2$$

Zinc oxid, ZnO, like other oxids generally, is formed by heating the hydroxid, carbonate, nitrate, sulfid, acetate and salts of other organic acids, or by heating other salts with Na_2CO_3. It is a white substance turning yellow on heating. When heated before the blowpipe after being moistened with a drop of dilute $Co(NO_3)_2$ a green color appears, Rinnmann's green, which is probably due to the formation of cobalt zincate, $CoZnO_2$.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all zinc compounds are reduced to the metal which is immediately volatilized and oxidized, forming on the charcoal a coating of the oxid, yellow when hot and white when cold.

Zinc salts contain the metal always in the bivalent condition. It acts as a base-forming element of about the same strength as ferrous iron, cobalt and nickel. Zinc compounds are generally colorless. The salts of the common laboratory acids are soluble and in solution are hydrolyzed but little; hence from cold solutions zinc hydroxid is not precipitated by the addition of $BaCO_3$ as is the case with the salts of the trivalent metals like ferric iron. (See page 225.)

The simple **zinc ion** is $\overset{++}{\mathbf{Zn}}$. Complex ions, zinc-ammonia and others, are known, also the zincate ion, $\overset{-}{\mathrm{ZnO}}_2$, in which zinc acts as an acid-forming element.

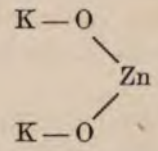
For the reactions of the $\overset{++}{\mathrm{Zn}}$ ion, any soluble simple salt will serve. The nitrate, $Zn(NO_3)_2.6H_2O$, is deliquescent as is the acetate,

---

* *Under proper* conditions Mg will throw Zn out of solutions of its salts.

$Zn(C_2H_3O_2)_2.7H_2O$. Each is extremely soluble and will melt in its own water of crystallization at temperatures but little above the ordinary.

The **hydroxyl ion, $\overset{-}{OH}$,** precipitates white ZnO_2H_2 which shows both acidic and basic properties. (See page 22.) In the presence of acids, it separates into $\overset{++}{Zn}$ and $\overset{-}{OH}$ ions, the latter uniting with the $\overset{+}{H}$ ions of the acids to form water, and leaving in solution the ions necessary to form zinc salts. On the other hand, the presence of a high concentration of $\overset{-}{OH}$ ions, the ionization of ZnO_2H_2 into $\overset{-}{OH}$ ions is repressed and $\overset{+}{H}$ and $\overset{=}{ZnO}_2$ ions are formed instead. In this case $\overset{+}{H}$ ions from zinc hydroxid and $\overset{-}{OH}$ ions from the base unite to form H_2O and leave in solution the ions necessary to form zincates. Alkali zincates are well-known, readily soluble salts of the type indicated by the formula



Because of the formation of these salts, all zinc compounds except ZnS dissolve readily in the strong alkalies.

Zinc hydroxid is soluble in NH_4OH forming, not ammonium zincate, but complex zinc-ammonia compounds, giving complex ions, $\overset{++}{Zn}(NH_3)_6$, exactly analogous to the cobalt-ammonia compounds (see page 229). Because of the formation of these bodies, all zinc compounds except ZnS and $Zn_2(Fe{=}C_6N_6)$ dissolve readily in NH_4OH.

With NH_4Cl and other ammonium salts, zinc hydroxid and other zinc salts form double salts of the type, $(NH_4)_2ZnCl_4$, which in fairly strong solutions, at least, dissociate into $\overset{+}{NH}_4$ ions and $\overset{=}{ZnCl}_4$. On diluting, simple ions are formed by decomposition of the complex ions. These compounds are characteristic of ferrous iron, cobalt, nickel, manganese and magnesium as well as of zinc and, because of their formation, in the presence of NH_4Cl no precipitate is given by any of these metals* when treated with NH_4OH or $(NH_4)_2CO_3$.

The **carbonate ion, $\overset{=}{CO}_3$,** causes a precipitate of varying composition, apparentaly consisting of much $Zn(OH)_2$ with some $ZnCO_3$.

The **sulfid ion, $\overset{=}{S}$,** precipitates from solutions neutral, alkaline, or acid with acetic acid only, white ZnS, readily soluble in the dilute mineral acids. In neutral solutions, the precipitation is not complete because of the liberation of mineral acid which causes the reaction to come to equilibrium, as indicated by the equation:

---

* Manganese gives a precipitate with $(NH_4)_2CO_3$ (see page 217).

$$ZnCl_2 + H_2S \leftrightarrow \mathbf{ZnS} + 2HCl$$

If sodium or other soluble acetate be added, the precipitation is complete. By the interaction of the strong acid with the acetate, acetic acid is set free. In acetic acid ZnS is insoluble.

The **sulfate ion, $\overline{\overline{\mathbf{S}}}\mathbf{O}_4$**, causes no precipitate since the sulfate is soluble in its own weight of water. From solution it separates with $7H_2O$ in the form characteristic of the "vitriols" (see page 188). It effloresces and may be preserved more satisfactorily than other zinc salts which are generally deliquescent. As "white vitriol," it finds many applications.

The **chlorid ion, $\overline{\mathbf{Cl}}$**, produces no precipitate, for zinc chlorid is extremely soluble. It melts readily and is volatile at a red heat. Its solutions show a tendency to become cloudy because of the formation of a basic salt due to hydrolysis.

The **cyanid ion, $\overline{\mathbf{C}}\mathbf{N}$**, precipitates white $Zn(CN)_2$, soluble in moderately concentrated mineral acids. It dissolves readily in an excess of alkaline cyanids, forming complex cyanids which dissociate into alkali and $(Zn\overline{\overline{C}}_4N_4)$ ions. These ions are quite unstable and decompose considerably into the simple ions in solutions of ordinary concentration.

The **ferrocyanid ion, $(\mathbf{Fe}=\overline{\overline{\overline{\overline{\mathbf{C}}}}}_6\mathbf{N}_6)$**, precipitates $Zn_2(Fe=C_6N_6)$, white in color and insoluble in dilute acids and NH_4OH. By alkalies it is decomposed, however, into alkaline zincates and ferrocyanids.

The **ferricyanid ion, $(\mathbf{Fe}\equiv\overline{\overline{\overline{\mathbf{C}}}}_6\mathbf{N}_6)$**, precipitates yellowish-white $Zn_3(Fe\equiv C_6N_6)_2$, insoluble in dilute acids.

The **phosphate ion, $\overline{\overline{\overline{\mathbf{P}}}}\mathbf{O}_4$**, precipitates white $Zn_3(PO_4)_2$, soluble even in acetic acid.

CADMIUM. Cd — 112.4.

Cadmium is a rather soft, white metal, resembling zinc very closely in appearance and properties. It is not appreciably tarnished by the constituents of the atmosphere at ordinary temperatures but, when heated, unites with oxygen, producing a vigorous combustion and giving off clouds of brown smoke consisting of the oxid, CdO.

The **metal** dissolves slowly in dilute mineral acids, HNO_3 being, as is usual, the most satisfactory solvent. In the passage from the metallic into the ionic condition some energy is liberated, hence **cadmium salts** are stable and not particularly easy of reduction. They are generally colorless and for the most part insoluble. Of the common salts the *nitrate, sulfate,* acetate and the halids are readily soluble.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all cadmium salts are reduced to the metal. A metallic globule is not obtained, however, because cadmium is volatilized. As the hot vapor moves away from the heated charcoal, it oxidizes rapidly, forming a brown coating on any cold surface.

The ordinary **cadmium ion** is **$\overset{++}{Cd}$**, furnished in abundance by solutions of the nitrate or other soluble salt with the exception of the halids. These cadmium compounds dissociate to a much smaller degree than do salts generally (see footnote, page 21). Complex ions formed by the union of the simple $\overset{++}{Cd}$ ion with NH_3, and with the $\overset{-}{CN}$ ion also, are well known.

The **hydroxyl ion, $\overset{-}{OH}$,** added to a solution containing the $\overset{++}{Cd}$ ion, produces a precipitate of white $Cd(OH)_2$. It is insoluble in an excess of NaOH or other reagent furnishing $\overset{-}{OH}$ ions in high concentration, being in this way differentiated from two other white hydroxids, $Zn(OH)_2$ and $Pb(OH)_2$, which are soluble. In the presence of free NH_3, complex ions are formed of which the best known is $\overset{++}{Cd}(NH_3)_4$. Since the compounds formed by this ion are generally soluble, $Cd(OH)_2$ dissolves in an excess of NH_4OH, thus showing a similarity to zinc and copper and difference from lead.

The hydroxid is soluble in alkaline cyanids forming soluble complex cyanids.

On heating, white $Cd(OH)_2$ breaks down into brown CdO and water, as all hydroxids do.

The **carbonate ion, $\overset{=}{CO}_3$,** precipitates white $CdCO_3$ which, on heating, breaks down into the brown CdO, as all except carbonates of the alkali metals do.

The **sulfid ion, $\overset{=}{S}$,** precipitates yellow CdS from neutral and alkaline solutions and, also, from solutions that contain only a small concentration of $\overset{+}{H}$ ions. The sulfid is soluble in a concentration of $\overset{+}{H}$ ions greater than is given by a 4 per cent. solution of HCl, hence CdS is not precipitated in the presence of much strong acid. Cadmium sulfid is not soluble in $(NH_4)_2S.xS$ and in this way may be differentiated from the yellow sulfids of arsenic, antimony and tin, all of which are soluble in yellow ammonium sulfid.

From slightly acid solutions of $CdCl_2$, an orange compound having the proportions represented by the formula $CdS.CdCl_2$ is first precipitated but is later changed into the pure yellow CdS.

The **sulfate ion, $\overset{=}{SO}_4$,** produces no precipitate since $CdSO_4$ is readily soluble. The crystallized salt ordinarily has the formula $(CdSO_4)_3.8H_2O$ but it may crystallize in the characteristic form of the "vitriols." $CdSO_4.7H_2O$.

The **chromate ion, $\mathbf{\overline{Cr}O_4}$**, causes no precipitate, as $CdCrO_4$ is soluble.

The **chlorid ion, $\mathbf{\overline{Cl}}$**, causes no precipitate, as $CdCl_2$ is soluble. It crystallizes with $2H_2O$. The bromid and iodid are similar.

The **cyanid ion, $\mathbf{\overline{CN}}$**, precipitates white $Cd(CN)_2$, soluble in acids, NH_4OH and an excess of alkaline cyanid, forming a double cyanid of the type $Na_2CdC_4N_4$, which gives rise to the complex ion, $(Cd\overline{\overline{C}}_4N_4)$. This ion is not very stable and even in concentrated solutions decomposes to a considerable extent into the simple $\overset{++}{C}d$ and $\overline{C}N$ ions. Hence, when H_2S is passed into the solution, CdS is precipitated, as is always the case when $\overset{++}{C}d$ and $\overline{\overline{S}}$ ions come together in neutral or alkaline solutions. In this particular, cadmium differs from copper which forms a similar double cyanid of the type $Na_3CuC_4N_4$, giving rise to the complex cyanid ion, $(Cu\overline{\overline{\overline{C}}}_4N_4)$. The latter is very stable; in solutions of fair concentration it does not dissociate appreciably into the simple ion and, therefore, is not precipitated by H_2S.

The **ferrocyanid ion, $\mathbf{(Fe=\overline{\overline{\overline{\overline{C}}}}_6N_6)}$**, precipitates white $Cd_2(Fe=C_6N_6)$, insoluble in dilute acids. Fairly concentrated acid readily dissolves it and NH_4OH does also.

MERCURY (Hydrargyrum). Hg — 200.

Mercury is the only metallic element liquid at ordinary temperatures. It melts at — 39.4° and boils at 357°. It is very heavy, possesses a silvery-white lustre and alloys readily with most other metals.* Mercury alloys are known as amalgams.

The metal does not tarnish in the air at ordinary temperatures but does unite slowly with oxygen when near the boiling-point. At a higher temperature the red HgO is decomposed into the elements.

Mercury is but little soluble in HCl or dilute H_2SO_4 for two reasons. First, the metal does not pass easily into the ionic condition and, therefore, does not take the charge from hydrogen ions readily. Secondly, what little action HCl and H_2SO_4 have on the element results in the formation of insoluble coatings of $(HgCl)_2$ or Hg_2SO_4, which protect the metal from further action. Oxidizing agents, such as HNO_3 and hot concentrated H_2SO_4, dissolve the metal readily, however. (Note similar action of acids on copper, page 79.)

When mercury and HNO_3 are brought together, the temperature and the relative proportions of acid and metal determine the reaction product. If mercury is present in excess and the acid is dilute and cold, mercurous nitrate, $(HgNO_3)_2$, is formed. If the HNO_3 is in excess,

---

* *Iron and platinum do not* alloy with mercury at ordinary temperatures.

$(HgNO_3)_2$ is oxidized to mercuric nitrate, $Hg(NO_3)_2$, especially if the acid is at all concentrated or heated.

Since mercury shows a disinclination to pass into the ionic condition and absorbs considerable energy when it assumes the electric charge, many other metals will precipitate the element from solutions of its salts because these metals show a stronger tendency to form ions than mercury does. Zinc, iron and copper precipitate the metal with great readiness. Mercury will throw down metallic silver, gold and platinum, however, from solutions of their salts.

Mercury salts, for this reason, are easily reduced to the metal by strong reducing agents. Heat alone is sufficient to decompose them in most instances. On the contrary, quite a number of mercury salts sublime without decomposition. By the addition of Na_2CO_3, however, all salts decompose when heated in a closed-tube, and mercury distills out of the mixture and collects on the cooler portions of the tube.

Mercury salts are of two general types; mercuric, in which the element is bivalent, and mercurous, in which the element may be considered as univalent. At ordinary temperatures, however, the molecules of mercurous salts seem to be doubled. Mercurous nitrate, for instance, is represented by the formula $(HgNO_3)_2$ rather than by $HgNO_3$, and other salts have corresponding double molecules. (See also page 83.)

Mercuric compounds are stable and frequently colorless. Salts of the common laboratory acids are soluble and generally separate from solution without water of crystallization.

Mercurous compounds are often unstable and show a decided tendency to change into the mercuric condition. They are usually much less soluble than the corresponding mercuric forms.

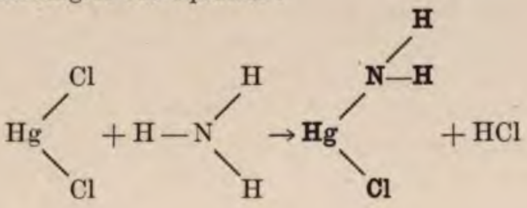
Mercury ions are of two types corresponding to the two classes of salts, the mercurous ion, $(\overset{+}{Hg})_2$, and the mercuric ion, $\overset{++}{Hg}$, being the most important. Since the compounds formed by the mercurous ion are entirely distinct from the compounds of the mercuric ion, they will be treated separately.

The Mercuric Ion, $\overset{++}{Hg}$.

For the reactions of the mercuric ion, solutions of the sulfate, acetate or chlorid may be used, but the nitrate is possibly most satisfactory. It crystallizes from solutions in the form $(Hg(NO_3)_2)_2.H_2O$.

The **hydroxyl ion, $\overset{-}{OH}$,** added to a solution containing the $\overset{++}{Hg}$ ion, doubtless forms $Hg(OH)_2$ in the first place, but this compound breaks down immediately into H_2O and yellow HgO. This precipitated product differs in color from a red compound having the same composition formed by heating the metal in air. By boiling with an excess of strong alkali, the yellow modification is changed over into the red. Mercuric oxid turns black on heating, but becomes red again on cooling.

If NH_4OH is used as a precipitant, a white precipitate falls in place of the yellow HgO, for the $\overset{++}{Hg}$ ion reacts with the NH_3 (which is always present as a decomposition product of NH_4OH) to form complex ions of which the mercuric-amido, $\overset{+}{Hg}NH_2$ is the best known. Its formation takes place according to the equation:



or, writing the ionic equation:

$$\overset{++}{Hg} + NH_3 \rightarrow \overset{+}{Hg}NH_2 + \overset{+}{H}$$

Since the salts formed by this ion are more insoluble than HgO, they are formed in preference. Mercuric amido-chlorid, $HgNH_2Cl$, taken as a typical salt, is white and insoluble in acids.

The **carbonate ion, $\overset{=}{CO}_3$**, precipitates yellow-brown $HgCO_3$, an unstable compound which, slowly at ordinary temperatures, rapidly on heating, loses its CO_2 and becomes HgO. If $(NH_4)_2CO_3$ be used as a precipitant, the $\overset{++}{Hg}$ ion reacts by preference with the NH_3 present in solution because of hydrolysis (see page 76) and the same salt is precipitated as with NH_4OH.

The **sulfid ion, $\overset{=}{S}$,** precipitates black HgS from alkaline and acid solutions as well. In the presence of considerable acid, especially HCl, a white precipitate having the proportionate composition $HgCl_2.2HgS$ first falls. On further treatment with H_2S, this passes through yellow, orange and red to the black sulfid.

On heating, HgS sublimes and changes to the red form, cinnabar, the sulfid found in nature and known as the pigment "vermilion."

Mercuric sulfid is insoluble in acids, alkalies and ammonium sulfid. It is readily soluble in the sulfids of the "fixed" alkali metals, however, according to the equation:

$$\mathbf{HgS} + K_2S \rightarrow K_2HgS_2$$

In concentrated solution the ions of this double sulfid are $\overset{+}{K}$ and $H\overset{-}{g}S_2$. On diluting, $H\overset{-}{g}S_2$ decomposes into the simple ions $\overset{++}{Hg}$ and $\overset{=}{S}$ and HgS is again precipitated.

By long continued action of boiling HNO_3 on HgS, it may be partially oxidized and form white $Hg(NO_3)_2.2HgS$. Aqua regia oxidizes this white compound as well as the black HgS readily to $HgCl_2$ and H_2SO_4.

The **sulfate ion, $S\overset{=}{O}_4$**, causes no precipitate, since $HgSO_4$ is readily soluble. With all the mercury salts of acids containing oxygen, there is a tendency, more marked in the mercurous than in the mercuric condition, toward the formation of insoluble oxysalts of the type $HgO.HgSO_4$. In dilute solutions free from acid, the mass action of the water causes appreciable hydrolysis of the salts into the weak base, $Hg(OH)_2$, which decomposes into HgO, as previously discussed. This combines with the normal salt to form insoluble oxysalts, which are thus seen to be dehydrated basic salts (see page 21). The addition of a little acid to the solution prevents the mass action of the water, however.

The **chromate ion, $Cr\overset{=}{O}_4$**, precipitates yellow $HgCrO_4$ from concentrated solutions, or possibly a red oxysalt. Both dissolve in the strong acids.

The **chlorid ion, $\overset{-}{Cl}$**, causes no precipitate since $HgCl_2$, "corrosive sublimate," is soluble in about 15 parts of water at ordinary temperatures and in less than two parts at 100°.

The **bromid ion, $\overset{-}{Br}$**, gives no precipitate since $HgBr_2$ is soluble.

The **iodid ion, $\overset{-}{I}$**, precipitates yellow HgI_2, changing rapidly to a red modification. Both forms are soluble in an excess of an alkaline iodid forming a complex ion, the alkaline salts of which are soluble. A typical salt of the proportionate composition $HgI_2.2KI$ dissociates into $\overset{+}{K}$ and $H\overset{-}{g}I_4$ ions, showing that a new compound has actually been formed. An alkaline solution of this salt turns brown in the presence of traces of NH_3 and, as the "Nessler reagent," is used to detect small amounts of ammonia in drinking water. All the mercury halids show a great tendency toward the formation of complex ions of this same type with the halids of other metallic elements. (See also similar lead salts, page 145.)

The **cyanid ion, $\overset{-}{CN}$**, precipitates white $Hg(CN)_2$ from concentrated solutions containing the $\overset{++}{Hg}$ ion, provided that halogen ions be not present. If KCN be added to $HgCl_2$, no precipitate falls, owing to the formation of some one of a series of double salts similar to those noted above.

The mercuric halids are of interest because of the fact that they ionize to a very small degree, a very marked point of difference between the behavior of these and of most other salts. Mercuric cyanid separates so few ions that a saturated solution conducts the electric current only a trifle better than pure water. The tendency toward dissociation is somewhat greater in the iodid and increases as the atomic weight of the halogen decreases. (See footnote, page 20.)

The **stannous ion, $\overset{++}{\mathbf{Sn}}$,** in $SnCl_2$ solution, causes the precipitation of white $(HgCl)_2$ or black Hg, depending on the proportions in which the reagents are present. The changes are caused by reduction, as the equations show:

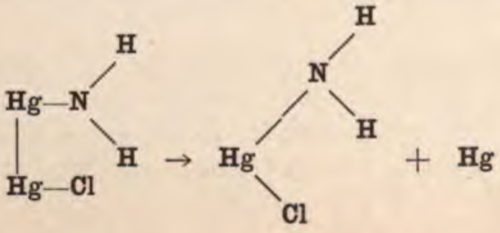
$$2HgCl_2 + SnCl_2 \rightarrow (HgCl)_2 + SnCl_4 \qquad HgCl_2 + SnCl_2 \rightarrow Hg + SnCl_4$$
$$2\overset{++}{Hg} + \overset{++}{Sn} + 2\overset{-}{Cl} \rightarrow (HgCl)_2 + \overset{++++}{Sn} \qquad \overset{++}{Hg} + \overset{++}{Sn} \rightarrow Hg + \overset{++++}{Sn}$$

The Mercurous Ion, $(\overset{+}{Hg})_2$.

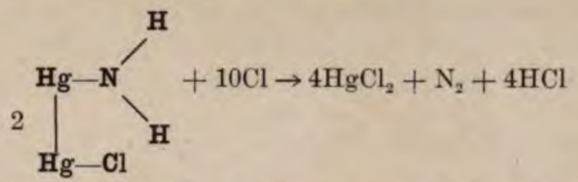
The mercurous ion, $(\overset{+}{Hg})_2$, is found in appreciable quantities only in solutions of the nitrate, $(HgNO_3)_2$, which is the only readily soluble compound formed by this ion. It separates from solutions with two molecules of water of crystallization. Because of hydrolysis, neutral solutions on standing separate, as a yellow powder, a basic nitrate, $(HgOH)_2(HgNO_3)_2$. The formation of this precipitate may be prevented by the addition of a little HNO_3. In order to prevent oxidation to the mercuric condition, metallic mercury must be present also, the excess of metal maintaining the salt in the lower form.

The **hydroxyl ion, $\overset{-}{\mathbf{OH}}$,** added to a solution containing the mercurous ion, $(\overset{+}{Hg})_2$, probably forms in the first place $(HgOH)_2$, but this immediately separates water and precipitates black Hg_2O. Mercurous oxid is very unstable, however, and soon breaks down into HgO and black Hg.

With NH_4OH, the $(\overset{+}{Hg})_2$ ion reacts analogously to the $\overset{++}{Hg}$ ion. A mercurous amido-chlorid, or other amido-salt, is first formed which is black in color. Like most mercurous salts, it decomposes into the corresponding mercuric compound and the free metal, as the equations indicate:



The black precipitate is insoluble in acids, but is oxidized by aqua regia to mercuric chlorid according to the equation:



$$2\left(\begin{array}{l}\mathrm{Hg{-}N}\begin{array}{l}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{array}\\ \,|\\ \mathrm{Hg{-}Cl}\end{array}\right) + 10\mathrm{Cl} \rightarrow 4\mathrm{HgCl_2} + \mathrm{N_2} + 4\mathrm{HCl}$$

The **carbonate ion, $\overset{=}{CO_3}$**, precipitates yellow Hg_2CO_3 which soon darkens, owing to decomposition into Hg_2O and CO_2 and then further into HgO and Hg. Ammonium carbonate causes the same precipitate as ammonium hydroxid because of the NH_4OH formed by the hydrolysis of the carbonate.

The **sulfid ion, $\overset{=}{S}$**, precipitates black Hg_2S. Since mercurous sulfid is not stable above zero, it ordinarily decomposes into HgS and Hg.

The **sulfate ion, $\overset{=}{SO_4}$**, precipitates white Hg_2SO_4 which, being somewhat soluble, may not fall in dilute solutions.

The **chromate ion, $\overset{=}{CrO_4}$**, causes red Hg_2CrO_4 to fall, soluble in HNO_3 but insoluble in alkaline hydroxids.

The **chlorid ion, $\overset{-}{Cl}$**, causes a granular precipitate of white $(HgCl)_2$, soluble in about 300,000 parts of H_2O and only a little more soluble in acids and alkalies. Mercurous chlorid is known medicinally as calomel. It is changed by NH_4OH into the black amido-chlorid noted above. Aqua regia oxidizes $(HgCl)_2$ into the soluble $HgCl_2$.

The **bromid ion, $\overset{-}{Br}$**, precipitates yellowish-white $(HgBr)_2$.

The **iodid ion, $\overset{-}{I}$**, causes green $(HgI)_2$ to precipitate. The original color soon darkens considerably, owing to the separation of metallic mercury and the formation of HgI_2, which dissolves in an excess of an alkaline iodid.

The **cyanid ion, $\overset{-}{CN}$**, forms in the first place $(HgCN)_2$, but this immediately decomposes into $Hg(CN)_2$ and Hg.

The **stannous ion, $\overset{++}{Sn}$**, from $SnCl_2$ solution, at first causes the precipitation of $(HgCl)_2$ because of the presence of the $\overset{-}{Cl}$ ion. Subsequently the $\overset{++}{Sn}$ ion reduces white $(HgCl)_2$ to black Hg. It is itself oxidized to the $\overset{++++}{Sn}$ ion at the same time. (See page 110.)

Group 3, First Type.

Boron 11; **Aluminum 27.1;** Scandium 44.1; Yttrium 89; Lanthanum 138.9.

This group consists of trivalent elements, in nature intermediate between the strong base-formers and the strong acid-formers. The hydrids are unimportant. The oxids of the elements with low atomic weights are anhydrids of weak acids, while the oxids of the elements with higher atomic weights unite with water, only indirectly, to form hydroxids which are weak bases. Compounds are generally colorless and stable, and it is only with difficulty that the element may be obtained from them.

The first two elements only are at all common. The hydroxid of boron acts normally as an acid. Aluminum hydroxid acts characteristically as a weak base, although it sometimes shows acid properties. This striking difference only illustrates the general rule to be observed in all groups, however, viz., that, as the atomic weight rises, base-forming properties develop and acid-forming qualities disappear.

BORON, B — 11.

The element **boron** is known as an amorphous brown powder which does not melt at the highest temperature of the electric arc. It dissolves considerably in molten aluminum, from which it separates in the form of exceeding hard and brilliant crystals that are much less reactive than the amorphous modification. At ordinary temperatures either form is stable but, when heated, each burns to the white oxid, B_2O_3.

Boron is not appreciably attacked by HCl. Hot concentrated H_2SO_4 or HNO_3 react with it, forming, possibly, a nitrate or sulfate (see also page 156), but these compounds (if they exist) are completely hydrolyzed into $B(OH)_3$ and the respective acids on diluting the solution.

Boron acts as a trivalent, acid-forming element, much weaker than nitrogen, phosphorous, arsenic or carbon. Its acid properties are more strongly developed than those of aluminum, however. The hydroxid, $B(OH)_3$, shows practically no basic properties and, therefore, is known as boric acid. All compounds of boron of any importance are derivatives of boric acid.

Compounds of boron give a distinct green color to a flame, provided the temperature be sufficiently hot to volatilize them. A Bunsen flame is scarcely hot enough and a blowpipe is needed to develop this color. On moistening with H_2SO_4, most boron compounds will be sufficiently decomposed into boric acid to give this reaction, but some silicates containing boron require the stronger decomposing action of hydrofluoric acid. (See page 135.)

Boric Acid.

Ortho-boric acid, H_3BO_3, has such weakly acidic properties that its solution conducts the electric current but little better than distilled water and gives only faint reaction to litmus. Its solubility increases rapidly with the temperature and from boiling aqueous solutions, on cooling, it separates in gleaming white scales. On heating to 100°, H_3BO_3 loses water, becoming meta-boric acid, HBO_2. At 160°, from four molecules of HBO_2 one molecule of water passes off, forming $H_2B_4O_7$, tetra-boric acid, which, at a higher temperature, breaks down into the anhydrid B_2O_3, a deliquescent vitreous substance.

On standing with water, all of these dehydration products become hydrated again, so that ortho-boric acid is the form ordinarily existing in and obtained from solution.

Salts of ortho-boric acid are not definitely known. If they exist at all, they are decomposed by water into free boric acid and salts of meta- and tetra-boric acids. The conditions of the experiment determine the character of the precipitate that will fall when a salt of a metal is added to a solution containing boric acid ions. From dilute solutions salts of the meta- type are precipitated most generally, independent of the nature of the boric acid compound used in making the solution, thus:

$$Na_2B_4O_7 + CaCl_2 + 3H_2O \rightarrow \mathbf{Ca(BO_2)_2} + 2NaCl + 2H_3BO_3$$

Sodium tetra-borate, or borax, $Na_2B_4O_7.10H_2O$, is the most important salt of boric acid. On heating, it intumesces as the water boils out and then fuses to a clear, colorless glass, known as "borax glass." This anhydrous borax has the power of dissolving metallic oxids, probably forming metaborates, many of which are very characteristically colored. A typical reaction might be written:

$$\mathbf{Na_2B_4O_7} + \mathbf{CoO} \rightarrow 2NaBO_2 + \mathbf{Co(BO_2)_2}$$

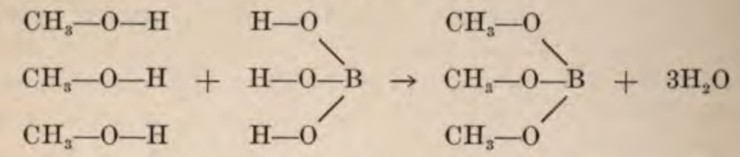
Borax-bead reactions furnish important information in blowpipe analysis. (See page 247.)

Borates of the alkali metals are soluble in water. Other borates are but little soluble in water; but, being salts of a very weak acid, they are readily dissolved by dilute inorganic acids. Ammonium chlorid has a decided solvent action, exerting a strong influence in holding up precipitates, often preventing their formation even in ammoniacal solutions.

Borates are readily transposed by boiling with sodium carbonate; barium meta-borate, for instance, giving barium carbonate and sodium borate.

Salts of boric acid, as well as the anhydrid, are extremely stable, and are not volatile except at high temperatures. Consequently, on fusion, neither the acid nor its salts are removed or appreciably changed. Curiously enough, however, boric acid is volatile in steam and significant loss may occur by the prolonged boiling of an acid solution before it comes to dryness.

Boric acid unites with the organic base, methyl alcohol, forming a salt, methyl borate, which is readily volatile.



This reaction takes place most satisfactorily in the presence of concentrated sulfuric acid which not only sets free the boric acid, but also unites with the water formed during the process, thus preventing a reversal of the reaction. On warming, methyl borate passes off with any excess of alcohol. On burning the vapor, methyl borate is oxidized to boric acid, carbon dioxid and water, thus:

$$2(CH_3)_3BO_3 + 9O_2 \rightarrow \mathbf{B_2O_3} + 9H_2O + 6CO_2$$

The boric anhydrid thus formed gives the characteristic green boron flame. Since, however, the temperature necessary for the development of this color is quite high, it is more satisfactory to burn the vapor in an apparatus which is essentially an improvised Bunsen burner. Into the mouth of the test-tube containing a borate, methyl alcohol and sulfuric acid, fit a stopper pierced by a glass tube which is drawn to a fine point. Support above this orifice a piece of glass tubing two to four inches long and a quarter of an inch in diameter, in such a position that when the vapors issue from the test-tube in the form of a jet, they will draw into the upper tube a supply of air. The mixture may be inflamed at the top of the upper tube, the increased amount of air producing a more perfect combustion, and developing a higher temperature, as in the case of the ordinary Bunsen burner.

When **turmeric paper** is dipped into a solution containing a borate acidified with HCl and is then dried at the temperature of boiling water, the yellow color of the turmeric paper is changed to pink or red. Alkaline solutions change the red to a greenish-black color.

The **barium ion, $\overset{++}{\mathbf{Ba}}$,** precipitates from solutions containing the borate ion, white, floccy barium meta-borate, $Ba(BO_2)_2$. It is readily soluble in acids and in ammonium chlorid.

The **silver ion, $\overset{+}{\mathbf{Ag}}$,** precipitates white silver meta-borate, $Ag(BO_2)_2$. soluble in dilute nitric acid and and in ammonium hydroxid.

ALUMINUM. Al — 27.1.

Aluminum is a light, silver-white, malleable metal. It is apparently not acted on by the atmosphere but, in reality, a thin compact coating of aluminum oxid is readily formed which, being very resistant to chemical agents generally, protects the metal from further action.

The metal dissolves readily in HCl and slowly in H_2SO_4. In HNO_3 it is not appreciably soluble, however. This is possibly due to the oxidizing action of HNO_3, resulting in the formation of a protective coating of Al_2O_3. In solutions of the strong basic hydroxids, the metal dissolves with the liberation of hydrogen and formation of alkaline aluminates (See also page 102.)

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$$

With the exception of magnesium and the alkali metals, no element shows a greater tendency to pass into the ionic condition. Under appropriate conditions, practically all the other metals are precipitated from solutions of their salts. On the other hand, no metal or other reducing agent is able to precipitate aluminum from solutions of its salts. Even in the "dry way," the reduction is accomplished only at very high temperature and with considerable difficulty.

Aluminum oxid, "alumina," Al_2O_3, is a firm, white substance which, after strong heating, becomes very resistant to acids and requires fusion with an alkaline carbonate or acid sulfate to get it into solution. In nature, it occurs as the minerals, corundum or emery, and when clear and colored slightly with other oxids, as the gems, sapphire and ruby.

Aluminum compounds are generally colorless. The salts of the common laboratory acids are all soluble and they hydrolyze decidedly in solution, since aluminum is a very weak base-forming element. To the fact that chromium and iron exist in the trivalent condition also and act as very weak base-forming elements is to be attributed largely the similar solubility relations because of which these three metals are classed together in qualitative analysis. A comprehensive survey of the properties of each element will not demonstrate any close relationship between aluminum and chromium and iron.

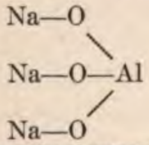
Heating before the **blowpipe** on charcoal with Na_2CO_3 produces only the oxid. If this be moistened with a drop of dilute $Co(NO_3)$ and reheated, a bright blue color, Thenard's blue, appears. Cobalt nitrate, like all nitrates, is decomposed on heating and forms the oxid which unites with Al_2O_3 to form the blue compound which is probably cobalt meta-aluminate, $Co(AlO_2)_2$. With the exception of the phosphate and silicate which require Na_2CO_3 to decompose them, all aluminum salts break down into Al_2O_3 on ignition. Except with the phosphate and silicate, therefore, this test may be made more satisfactorily by heating on porcelain or platinum without Na_2CO_3.

Of **aluminum ions** the only kathion is $\overset{+++}{Al}$. The metal enters as a constituent in certain anions of which the ortho-aluminate ion, $\overset{\equiv}{Al}O_3$, and the meta-aluminate ion, $\overset{-}{Al}O_2$, are the most important.

A solution of any of the ordinary soluble salts of aluminum will serve satisfactorily for the study of the reaction of the $\overset{+++}{Al}$ ion. The double sulfate of potassium and aluminum, ordinary alum, may also be used.

The **hydroxyl ion, $\overset{-}{OH}$,** precipitates white, gelatinous $Al(OH)_3$, which shows considerable tendency to form colloidal solutions. This is readily prevented by the presence of ammonium salts, however. When first precipitated, the hydroxid is readily soluble in dilute acids but, on standing in the solution, becomes less and less soluble, probably due to partial dehydration, for the oxid is much less soluble than the hydroxid. The properties of the naturally-occurring hydroxids confirm this supposition. Hydrargillite, $Al(OH)_3$, is readily soluble in hot HCl but beauxite, $Al_2O(OH)_4$, and diaspore, $AlO(OH)$, are insoluble in the same solvent.

Aluminum hydroxid possesses weak acid as well as basic properties (see page 22), and will dissolve in solutions of the strong alkalies, forming aluminates of which two types are recognized.



Sodium ortho-aluminate.

$$Na{-}O{-}Al{=}O$$

Sodium meta-aluminate.

Ammonium aluminate apparently exists, for $Al(OH)_3$ will dissolve somewhat in NH_4OH. The ammonium salt hydrolyzes very greatly and precipitates $Al(OH)_3$, especially on warming. This action is favored by the fact that NH_4OH decomposes under these conditions into NH_3 and H_2O and may be boiled off. This reduces the amount of NH_4OH below the concentration necessary to maintain equilibrium, hence the reaction ceases to be reversible and all of the aluminum may be precipitated from solution.

$$(NH_4)_3AlO_3 + 3H_2O \rightarrow \mathbf{Al(OH)_3} + 3\mathit{NH_3} + 3H_2O$$

The analogous precipitation of $Al(OH)_3$ from solutions of sodium or potassium aluminate can not be accomplished, for the $Al(OH)_3$ and alkali, as fast as formed, interact to regenerate the aluminate again.

$$Na_3AlO_3 + 3H_2O \leftrightarrow Al(OH)_3 + 3NaOH$$

By adding sufficient ammonium salt to the solution, however, ammonium aluminate and a sodium salt are formed, and $\mathrm{Al(OH)_3}$ is then precipitated.

$$\mathrm{Na_3AlO_3 + 3NH_4Cl \rightarrow (NH_4)_3AlO_3 + 3NaCl \rightarrow}$$
$$\mathbf{Al(OH)_3} + 3NH_3 + \mathrm{3H_2O + 3NaCl}$$

Cobalt meta-aluminate is probably the compound formed by heating CoO with $\mathrm{Al_2O_3}$. It is blue in color. Aluminates of calcium are among the compounds formed when Portland cement "sets."

In the presence of tartaric, citric, malic and other acids, sugars, starches and organic compounds containing the hydroxyl radicle, $\mathrm{Al(OH)_3}$ is not precipitated, owing to the formation of compounds which produce stable complex ions and not the simple $\overset{+++}{\mathrm{Al}}$ ion. Hence organic matter in general must be removed, usually by ignition, before aluminum can be precipitated as the hydroxid. (See also pages 193 and 224.)

The **carbonate ion, $\overset{=}{\mathbf{CO}}_3$,** precipitates $\mathrm{Al(OH)_3}$, this product being formed by complete hydrolysis of the carbonate which is probably the substance first formed.

The **sulfid ion, $\overset{=}{\mathbf{S}}$,** produces no precipitate in acid solution, for $\mathrm{Al_2S_3}$, formed only in the "dry way," is soluble in acids and is completely hydrolyzed by water into the hydroxid and $\mathrm{H_2S}$. Hence on introducing the $\overset{=}{\mathrm{S}}$ ion into solutions alkaline with $\mathrm{NH_4OH}$, aluminum hydroxid is precipitated.

The **sulfate ion, $\overset{=}{\mathbf{SO}}_4$,** produces no precipitate, for the sulfate, $\mathrm{Al_2(SO_4)_3}$, is readily soluble. This salt, like all the common soluble salts of aluminum, deliquesces greatly and, therefore, can not be well preserved. The double sulfate of aluminum and potassium, $\mathrm{Al_2(SO_4)_3.K_2SO_4.24H_2O}$, does not deliquesce, is very soluble (in about 15 parts $\mathrm{H_2O}$ at ordinary temperatures and less than one-third part $\mathrm{H_2O}$ at 100°) and is by far the most important salt of aluminum in the industrial world. It is to be regarded as the potassium salt of an aluminum-sulfuric acid and its formula is probably more correctly written $\mathrm{KAl(SO_4)_2.12H_2O}$. In concentrated solutions, it doubtless forms complex ions (possibly $\mathrm{Al(\overset{=}{SO}_4)_2}$) to a slight extent, but these are so unstable in dilute solutions that only $\overset{+}{\mathrm{K}}$, $\overset{+++}{\mathrm{Al}}$ and $\overset{=}{\mathrm{SO}}_4$ ions are in evidence. Hence an "alum" solution gives all the reactions of the $\overset{+++}{\mathrm{Al}}$ ion.

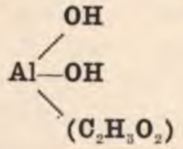
The term, "**alum,**" is used to designate a class of compounds of similar composition, all of which crystallize in the same form from solution. In place of aluminum, trivalent chromium, iron and manganese may be substituted. Sodium, ammonium and other univalent metals may replace potassium, while sulfur may be similarly substituted by the rarer elements, tellurium and selenium.

The **chlorid ion, $\bar{\mathrm{Cl}}$,** produces no precipitate, as aluminum chlorid, like other halids, is very soluble. The crystallized salt, $AlCl_3.6H_2O$, will dissolve in about one-fourth of its own weight of water. As an illustration of the strong tendency of aluminum salts to hydrolyze, it may be stated that a solution of $AlCl_3$ will, on evaporation, leave $Al(OH)_3$ entirely. The equilibrium in this case is prevented by the volatility of HCl which passes off with the water vapor. With salts of non-volatile acids, the introduction into the solution of some reagent, such as $BaCO_3$, that will lower the concentration of the free acid formed by hydrolysis, is sufficient to cause the reaction to run to completion.

The **cyanid ion, $\overline{\mathrm{CN}}$,** precipitates $Al(OH)_3$ because of hydrolysis. *No cyanids of trivalent metals are known.*

The **phosphate ion, $\overset{\equiv}{\mathrm{PO}}_4$,** precipitates white $AlPO_4$, readily soluble in dilute mineral acids. Like chromium and ferric phosphates, it is insoluble in acetic acid and, by this means, may be separated from the metals forming Groups III and IV of the qualitative analysis scheme. Like aluminum salts generally, it is readily soluble in the strong alkalies, forming alkaline aluminates and phosphates.

The **acetate ion, $(C_2\bar{H}_3O_2)$,** produces no precipitate, as aluminum acetate, $Al(C_2H_3O_2)_3$, is very soluble. By boiling a dilute solution the salt is about two-thirds hydrolyzed, and a precipitate is formed having approximately the proportions indicated by the formula,



It is known as a basic acetate (see also pages 194 and 226). On cooling the solution, the precipitate dissolves in the acetic acid formed by the hydrolysis. It is thus a distinctly reversible reaction with the equilibrium much modified by changes of temperature.

Group 3, Second Type.

Gallium 70; Indium 115; Thallium 204.1.

The members of this group are trivalent elements, in general resembling the other type, although they possess rather more metallic properties. As all of them are very rare substances, they will not be considered in detail.

Group 4, First Type.

Carbon 12; **Silicon 28.4**; Titanium 48.1; Zirconium 90.6; Cerium 140; Thorium 232.5.

This group, as a whole, is of intermediate character, possessing neither metallic nor non-metallic properties in a marked degree. Carbon and silicon only are of common occurrence and, since they are the members of lowest atomic weights, they show rather more non-metallic properties than the other rarer elements. Typical compounds are colorless and contain the element in the tetravalent condition. Compounds in which the element exhibits divalence are well known, however. Beginning with this group, the hydrids become of importance. They are neutral in character and do not unite with water. The oxids of the lower members are the anhydrids of very weak acids. The oxids of the other elements unite with water to form hydroxids, the higher ones acting as bases and those of medium atomic weights showing either acid or basic properties, depending on the environment. Compounds of these elements are strikingly similar in composition and, bearing in mind constantly the normal variation to be expected within each group, in properties also.

CARBON. C — 12.

The **element** exists in at least three allotropic modifications.

Diamond is the form obtained by crystallization at high temperatures under great pressure. It is usually clear and colorless, is the hardest known substance and is very resistant to all chemical action.

Graphite is a soft, gray-black substance, existing in the form of crystalline scales, which is almost as resistant to chemical action as diamond.

Amorphous carbon is known in the various forms: charcoal, coke, gas-carbon, bone-black, and soot or lampblack. All of these bodies are quite resistant, but not to the same degree as diamond and graphite. None of these allotropic forms melt under atmospheric pressure but, when heated to the highest temperature of the electric arc or furnace, it is just possible to make them sublime. All modifications may be made to unite with oxygen, *i. e.*, burn, by being strongly heated. The great ease with which carbon is oxidized makes it one of the best reducing agents for high-temperature reactions. In the form of coke or charcoal, it is much used to obtain metals from their ores. Carbon monoxid is a product of incomplete combustion but the dioxid is the final product.

Carbon monoxid, CO, is a colorless, poisonous gas, but little soluble in water. It unites with oxygen readily at higher temperatures forming the dioxid, thus acting as a good reducing agent. It burns with a blue flame.

Carbon dioxid, CO_2, is a colorless gas with a slight pungent odor and feebly acid taste. It is half again as heavy as air and fairly soluble in water, one volume of water dissolving somewhat more than an equal volume of gas. The solution has a slight acid reaction, hence carbon dioxid must be regarded as an acid anhydrid. It may be removed entirely from solution by boiling, however.

Carbon disulfid, CS_2, is an analogous body formed by direct union of the elements at a high temperature. It is a heavy liquid with a slight yellow color, boiling at 46°, and is practically insoluble in water. It is a good solvent for fats and oils and also for bromin, iodin and some other inorganic substances. It is quite volatile at ordinary temperatures and, as its vapors form an explosive mixture with air, it should never be used near a flame or heated substance.

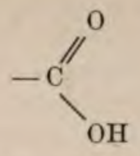
The **compounds of carbon** show that it acts as a weak acid-forming element, being for the most part tetravalent, although in certain compounds, which are more or less unstable and oxidize readily, it appears divalent. It unites with most metals to form carbids, many of which are decomposed by water or dilute acids with the liberation of hydrids. The chief characteristic of carbon is the almost limitless number of compounds which it forms with hydrogen, oxygen and a few other elements. These compounds constitute the field of **organic chemistry** which has come to mean simply *the chemistry of the carbon compounds.* The variation of properties found among these bodies is almost as great as that encountered in the inorganic world. Organic compounds are generally less stable, however, and, on heating out of contact with air, they decompose quite generally into carbon and other substances. When heated in the air, they burn to CO_2, H_2O and other oxidation products.

Compounds of carbon with hydrogen only are of several distinct classes, of which ethane, C_2H_6, ethylene, C_2H_4, acetylene, C_2H_2, benzene, C_6H_6, and naphthalene, $C_{10}H_8$, are the more important types. They are the hydrids of carbon commonly known as hydrocarbons. Certain combinations or radicles, such as $CH_3—$, $C_2H_5—$, etc., unite with other elements to give compounds analogous to those of the inorganic realm.

Organic oxids, compounds of these radicles with oxygen, are known as ethers. Of this class, ordinary ether, $C_2H_5 — O — C_2H_5$, is the most important.

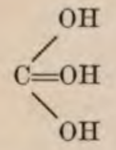
Organic hydroxids are known as alcohols. Of these, wood alcohol, CH_3OH, ordinary or ethyl alcohol, C_2H_5OH, and amyl alcohol, $C_5H_{11}OH$, are the most important.

Organic acids contain the group—

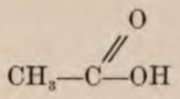


No acid of carbon is as strong as the common mineral acids. Some, however, dissociate to a greater degree than weak mineral acids, such as boric and silicic acids.

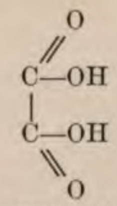
Carbonic, acetic, oxalic and tartaric acids are most important and have the composition and structure indicated by the formulae:



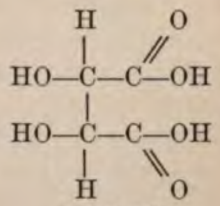
Carbonic acid.



Acetic acid.



Oxalic acid.



Tartaric acid.

Organic salts are formed by the interaction of an organic acid with an organic hydroxid or alcohol. They are known as esters and are characterized by sweet, agreeable odors. Many of the perfumes and flavoring extracts in general use belong to this class of compounds.

The acid compounds of carbon are of chief interest in analytical chemistry and the most important of these will be considered in greater detail.

Carbonic Acid, H_2CO_3.

Of the more common acids of carbon, carbonic acid is the weakest and most unstable. It has never been obtained free, since it immediately decomposes into water and the anhydrid, CO_2. That it does exist to a slight extent in aqueous solution, however, is indicated by the fact that carbon dioxid, passed into water, gives to it a slight acid reaction. Toward metallic hydroxids, it acts as a dibasic acid, forming salts of most of the metals, carbonates of arsenic, antimony, tin, chromium, aluminum and ferric iron alone being rare or unknown. Although more stable than the free acid, with the exception of the salts of the alkali metals, all *carbonates are decomposed on heating into* CO_2 *and an oxid of the metal.* Carbonates of the alkaline earths are most difficult to decompose, in this as in other ways showing their close relation to the alkali metals. Ammonium carbonate is volatile.

All normal carbonates, with the exception of those of the alkali metals and ammonium, *are comparatively insoluble in water,* but are readily decomposed by dilute acids. On treatment of a carbonate with any stronger acid, carbonic acid is set free and breaks down to a large extent into the anhydrid, CO_2, which passes out of solution. On boiling, the decomposition is completed and all carbon dioxid may be removed.

If CO_2 gas is passed into water containing insoluble carbonates of the elements of the alkaline-earth group (Ba, Sr, Ca, Mg) held in suspension, the precipitate dissolves, probably forming **acid carbonates** of the type $CaH_2(CO_3)_2$ (see page 95). These acid salts are soluble but are decomposed, on boiling, into the normal carbonate, water and carbon dioxid. The only acid carbonates known in the solid state are those of the alkali metals.

The **barium ion, $\overset{++}{Ba}$,** when brought into contact with **the carbonate ion, $\overset{=}{CO}_3$,** gives a floccy white precipitate, $BaCO_3$, which, on long standing or boiling, becomes crystalline. (See page 99.)

The **silver ion, $\overset{+}{Ag}$,** precipitates yellowish-white Ag_2CO_3. Like most silver salts, it is readily soluble in NH_4OH. Like all carbonates, it dissolves readily in HNO_3.

Acetic Acid, $H(C_2H_3O_2)$.

Acetic acid is a well-known monobasic acid of carbon. Since it is by no means as strong as the ordinary mineral acids, it may be set free from its salts by them. It mixes with water in all proportions and boils at 118°. Its salts, like *the salts of organic acids generally, are decomposed by heating into carbonates.* Hence, on ignition, the free acid may be volatilized and its salts destroyed. Fusion with ammonium nitrate oxidizes it completely.

All normal acetates are soluble in water, and are transposed by boiling with sodium carbonate.

The **common anion** is **$(C_2\overset{-}{H}_3O_2)$.**

The **barium ion, $\overset{++}{Ba}$,** produces no precipitate.

The **silver ion, $\overset{+}{Ag}$,** produces no precipitate except in concentrated solutions when white $Ag(C_2H_3O_2)$ falls. It is soluble in about 100 parts of H_2O at ordinary temperature.

The **ferric ion, $\overset{+++}{Fe}$,** added to a neutral solution of an acetate produces a deep red color, due to the formation of ferric acetate, $Fe(C_2H_3O_2)_3$, which, on abundant dilution and boiling, hydrolyzes partially, forming a precipitate of basic ferric acetate, $Fe(C_2H_3O_2)(OH)_2$, indistinguishable in appearance from ferric hydroxid. (See page 226.)

Ethyl alcohol unites with acetic acid to form ethyl acetate (see page 23), a compound characterized by a peculiar sweet, ethereal odor. With **amyl alcohol** a similar compound is formed which has the familiar banana odor. The formation of these compounds takes place most satisfactorily in the presence of concentrated sulfuric acid which should be warmed. Heating should be avoided, as hot concentrated sulfuric acid acts as an oxidizing agent (see page 187) and the sulfur dioxid formed will make the ethereal odor very difficult to detect.

Oxalic Acid, $H_2C_2O_4$.

Oxalic acid is a common dibasic acid of carbon, readily formed by the oxidation of organic matter with nitric acid. Since all organic acids are of much the same nature, it suggests acetic acid in some of its reactions. It is a white solid, readily soluble in water, from which it crystallizes with two molecules of water of crystallization. It is the strongest of the common acids of carbon, dissociating more than phosphoric but less than sulfuric acids (see page 16). On heating, it does not melt but sublimes readily. Its salts are generally not volatile and, when heated, they break down in carbonates. Hence, by ignition, the free acid may be removed and its salts destroyed.

Concentrated H_2SO_4, on heating, decomposes oxalic acid into water and equal volumes of carbon monoxid and dioxid.

$$\mathbf{H_2C_2O_4} \rightarrow H_2O + CO + CO_2$$

Oxalic acid may be readily oxidized to CO_2 and water, by fusion with ammonium nitrate or by treating its solution with a permanganate. Each molecule of oxalic acid absorbs one atom of oxygen and the reaction is therefore equivalent to the oxidation of CO to CO_2 (see page 47).

All oxalates are fairly insoluble with the exception of the salts of the alkali metals and of magnesium. They are readily soluble in dilute mineral acids, but not, as a rule, in acetic acid. In the presence of an excess of oxalic acid or an alkaline oxalate, soluble complex salts tend to form in many instances.

All oxalates are readily transposed by sodium carbonate, with the exception of salts of cobalt, nickel, manganese and zinc, which require long boiling.

The **common ion** is $\mathbf{C_2\overset{-}{O}_4}$.

The **calcium ion, $\overset{++}{\mathbf{Ca}}$,** causes a fine white precipitate of $CaC_2O_4.2H_2O$ which is exceedingly insoluble in water and dilute acetic acid. Being more insoluble (see page 97) than any other salt of calcium that will fall in the presence of acetic acid (see page 261), calcium oxalate will be precipitated when a solution containing oxalate ions is treated with a solution of calcium sulfate.

The **barium ion, $\overset{++}{\mathbf{Ba}}$,** precipitates white BaC_2O_4, soluble in dilute acids, even acetic acid.

The **silver ion, $\overset{+}{\mathbf{Ag}}$,** precipitates white, curdy silver oxalate, $Ag_2C_2O_4$, soluble in HNO_3 and in NH_4OH.

Tartaric Acid, $H_2(C_4H_4O_6)$.

Tartaric acid is another well-known, dibasic acid of carbon. In a general way it resembles the carbon acids already considered. It is a colorless solid, melting at 107°, readily soluble in water from which it crystallizes anhydrous. Unlike acetic and oxalic acids, free tartaric acid is not volatile, but is decomposed on heating with the separation of carbon and the production of an odor like that of "burnt sugar." This reaction, known as *"charring," is common to non-volatile organic matter in general,* and, as the phrase signifies, the "burnt sugar" odor is not peculiar to tartaric acid.

Hot concentrated sulfuric acid produces these same phenomena when brought in contact with many forms of organic matter, the concentrated acid aiding the decomposition by the abstraction of water. In addition, sulfur dioxid may be liberated. This gas is a reduction product of sulfuric acid which gives up its oxygen to the organic matter to form carbon dioxid and water, while H_2SO_4 becomes H_2SO_3, sulfurous acid. The latter, being unstable, separates its anhydrid, SO_2, which is volatile. *Reduction of hot concentrated sulfuric acid is characteristic of organic matter in general.*

Tartaric acid, like oxalic acid, is readily oxidized, either by fusion with ammonium nitrate or, in the "wet way," by permanganate. Carbon dioxid and water are the ultimate products of the oxidation but, in the "wet way," the reaction does not under all conditions run to the end.

Salts of tartaric acid are readily broken down on heating into carbonates of the metal, carbon dioxid, water and free carbon.

Tartrates of the alkalies, except acid potassium and acid ammonium tartrates (see pages 73 and 78), are readily soluble in water. Most other tartrates are quite insoluble but are dissolved on the addition of dilute acids.

All tartrates are transposed by boiling with sodium carbonate.

The **common ion** is $(\mathbf{C_4\overset{=}{H}_4O_6})$. Several complex anions are recognized which contain within them metallic elements such as copper, iron, aluminum and chromium. (See pages 81, 224, 117, 193.)

The **barium ion, $\overset{++}{\mathrm{Ba}}$,** added to a neutral solution containing the tartrate ion, produces a white flocculent precipitate of barium tartrate, $Ba(C_4H_4O_6)$, soon becoming crystalline. It is readily soluble in an excess of an alkaline tartrate, producing soluble double tartrates. It dissolves readily in acetic and other acids, and in strong alkali solutions forming the soluble double tartrates just mentioned.

The **calcium ion, $\overset{++}{\mathrm{Ca}}$,** acts similarly to the barium ion. Although calcium tartrate, $Ca(C_4H_4O_6)$, requires more than 5,000 parts of water for its solution, at ordinary temperatures it readily forms supersaturated solutions, from which the insoluble salt precipitates only on standing. Ammonium salts, especially the chlorid, tend to hold up the precipitate.

The **silver ion, $\overset{+}{\mathrm{Ag}}$,** precipitates silver tartrate, $Ag_2(C_4H_4O_6)$, from a neutral solution. It is readily soluble in dilute acetic acid and ammonium hydroxid. When the precipitated silver tartrate is dissolved in a few drops of ammonium hydroxid and warmed, the salt decomposes, precipitating metallic silver in the form of a brilliant mirror on the sides of the test-tube.

Cyanogen, $(CN)_2$.

Under the influence of the electric arc, carbon and nitrogen can be made to unite, forming cyanogen, $(CN)_2$, so named because of the deep blue color of some of the compounds it forms. Cyanogen is a colorless, poisonous gas with an odor or taste like "bitter almonds," burning with a characteristic lavender-pink flame. It is soluble in water. It unites with yellow ammonium sulfid according to the equation:

$$(NH_4)_2S.S + (CN)_2 \rightarrow 2(NH_4)SCN$$

In this way it may be changed into a thiocyanate and tested for, as directed on page 292.

Cyanogen resembles in a general way the less active members of the halogen group. Like chlorin, it reacts with solutions of the alkalies giving analogous compounds.

$$Cl_2 + 2KOH \rightarrow KCl + KOCl \qquad (CN)_2 + 2KOH \rightarrow KCN + KOCN$$

Like the halogens, also, it forms a compound with hydrogen which is acid in nature.

Hydrocyanic Acid, "Prussic Acid," HCN.

Hydrogen cyanid is a colorless liquid with an odor like "bitter almonds." It boils at 26° and freezes to an ice-like solid which melts at

—14°. It is readily soluble in water. Although showing unmistakable acid reactions, it stands near the extreme limit of the weak acids, dissociating so little in aqueous solution that the $\overset{+}{H}$ ions can scarcely be detected by litmus paper. It is unstable in solution, uniting with water to form formic acid, H(COOH) and ammonia, which tend to neutralize each other.

$$HCN + 2HOH \rightarrow H(COOH) + NH_3 = HCOO(NH_4)$$

The **cyanids** are a well-characterized series of salts of which the alkali, alkaline earth and the higher form of mercury are soluble in water. Some are soluble with difficulty. Others are so highly insoluble that they are not dissolved by dilute mineral acids, contrary to the general rule for salts of weak acids. *Cyanids of metals with a valence greater than two are unknown* (except in complex salts).

All cyanids are decomposed by hot concentrated sulfuric acid with the formation of sulfates. Some HCN is usually liberated but much is decomposed into CO and NH_3 according to the reaction:

$$\mathbf{Fe(CN)_2} + 2H_2SO_4 + 2H_2O \rightarrow FeSO_4 + (NH_4)_2SO_4 + 2\mathit{CO}$$

All cyanids are transposed by boiling with sodium carbonate.

Soluble cyanids hydrolyze to a great extent in solution because HCN is such a weak acid. On standing in the atmosphere, carbon dioxid is absorbed and carbonates of the metals result. Furthermore, decomposition of the hydrocyanic acid formed by the hydrolysis takes place, as already noted.

On heating out of contact with air, cyanids of the alkali metals fuse unchanged, while insoluble cyanids are converted either into (1) cyanogen and the metal, or (2) into a metallic carbid and nitrogen, or (3) entirely decomposed into their elements.

Cyanids are readily oxidized and are frequently used as reducing agents in blowpipe reactions. Each molecule of cyanid absorbs one atom of oxygen, as shown in the equation:

$$2\mathbf{KCN} + \mathit{O}_2 \rightarrow 2\mathbf{KOCN}$$

In alkaline solution, yellow ammonium sulfid or other reagent containing free sulfur oxidizes a cyanid to a thiocyanate. Since the ferric ion gives a deep red color with the thiocyanate ion due to the formation of ferric thiocyanate, $Fe(SCN)_3$, this procedure offers a good test for cyanids.

Many insoluble cyanids are soluble in solutions of alkaline cyanids, forming complex cyanids. Since many of these solutions respond but slightly or not at all to tests for the heavy metal present in them, indicating a great reduction in the concentration of the heavy metal ions, if not their entire absence, it is incorrect to consider these solutions as mixtures of the two cyanids. New compounds are formed—**complex cyanids**—dissociating into complex ions containing cyanogen united with heavy metals in various proportions. Four different types are well recognized, the metal and its valence being indicated by $M-$, $M=$, and $M\equiv$: $K-(M-C_2N_2)$, $K_2=(M=C_4N_4)$, $K_3\equiv(M\equiv C_6N_6)$, $K_4≣(M=C_6N_6)$. These bodies dissociate as salts of mono-, di-, tri- and tetrabasic acids as indicated, the heavy metals being contained in the complex anion and not existing in the form of simple kathions. These complex ions possess different degrees of stability and tend to decompose, more or less, into simple ions, equilibrium between the simple and complex ions being reached at different stages in the decomposition process.

The acids corresponding to the first two of the above types are so unstable that they decompose immediately into cyanids of hydrogen and the metal. Consequently, when salts of these types are acidified, hydrocyanic acid is liberated and the insoluble cyanid precipitated. To this class belong $K(Ag-C_2N_2)$, $K(Au-C_2N_2)$, $K(Cu-C_2N_2)$, $K_2(Hg=C_4N_4)$, $K_2(Cd=C_4N_4)$, $K_2(Ni=C_4N_4)$ and $K_2(Zn=C_4N_4)$. The different degrees of instability and of decomposition into simple metallic ions are illustrated by the different action of hydrogen sulfid on these salts, the precipitation of the sulfids taking place in proportion to the concentration of metallic ions present. From solutions of the silver, mercury and cadmium salts, the corresponding sulfids are precipitated practically completely; zinc salts give only a partial action while nickel salts give no precipitate at all.

Compounds of the third and fourth types are generally more stable. Although $K_4≣(Mn=C_6N_6)$ and $K_4≣(Co=C_6N_6)$ are decomposed by acidifying, yet $H_3\equiv(Co\equiv C_6N_6)$, $H_3\equiv(Fe\equiv C_6N_6)$ and $H_4≣(Fe=C_6N_6)$ are sufficiently stable to be isolated from solution. The complex iron cyanids are most important and will be considered in detail. (See pages 130 and 131.)

The **simple cyanid ion** is **$\overset{-}{CN}$**, for the reactions of which a solution of an alkaline cyanid serves most satisfactorily.

The **barium ion, $\overset{++}{Ba}$**, causes no precipitate.

The **silver ion, $\overset{+}{Ag}$**, precipitates yellowish-white AgCN, soluble in ammonium hydroxid and alkaline cyanids, but insoluble in nitric acid.

The **ferrous ion, $\overset{++}{Fe}$**, when introduced into a neutral or alkaline solution containing the $\overset{-}{CN}$ ion, reacts slowly in the cold, but rapidly on boiling, to form the complex ferrocyanid ion, $(Fe=\overset{≣}{C}_6N_6)$, according to equation:

$$6KCN + FeSO_4 \rightarrow K_4(Fe=C_6N_6) + K_2SO_4.$$

or written ionically

$$6\overset{-}{\mathrm{C}}\mathrm{N} + \overset{++}{\mathrm{F}}\mathrm{e} \rightarrow (\mathrm{Fe} = \overset{=}{\overset{=}{\mathrm{C}}}_6\mathrm{N}_6)$$

This affords a very delicate means of detecting the $\overset{-}{\mathrm{C}}\mathrm{N}$ ion since the ferrocyanid ion, when treated with the ferric ion, precipitates deep-blue ferric ferrocyanid, $\mathrm{Fe}_4(\mathrm{Fe}=\mathrm{C}_6\mathrm{N}_6)_3$. (See page 294.)

Cyanic Acid, HOCN.

Subjected to the action of oxidizing agents, salts of hydrocyanic acid take up oxygen, forming cyanates. Cyanic acid, HOCN, is a liquid with a very strong odor. It is stronger than hydrocyanic acid but not so stable, as it cannot exist in contact with water, but is broken up into carbon dioxid and ammonia.

$$\mathrm{HOCN} + \mathrm{H_2O} \rightarrow \mathrm{NH_3} + CO_2$$

Therefore, if dilute solutions of cyanates are treated with acids, carbon dioxid is the gas which is for the most part liberated, since ammonia unites with the excess of acid and remains in solution. From the fact that the cyanates evolve $\mathrm{CO_2}$ (possibly some undecomposed HOCN also) when treated with acids, they may be readily distinguished from the cyanids, which evolve HCN.*

The **salts of cyanic acid,** in sharp contrast to the instability of the free acid, are very stable even on heating. The alkali and alkaline earth salts are readily soluble; the silver, copper and lead and lower form of mercury salts are highly insoluble, other salts being soluble with difficulty. All cyanates are soluble in dilute mineral acids and are transposed by boiling with sodium carbonate.

When a not too dilute solution of a cyanate is treated with cobalt acetate, a blue color appears, due to the formation of potassium cobaltocyanate, $\mathrm{K_2(CoO_4C_4N_4)}$. In dilute solutions, this complex cyanate separates into the simple cyanates, and the blue color vanishes, to reappear on the addition of more cyanate or of alcohol which prevents the decomposition. This reaction is given by thiocyanates as well, but not by cyanids, nor by cyanates in the presence of cyanids.

The **barium ion, $\overset{++}{\mathrm{B}}\mathrm{a}$,** gives no precipitate.

The **silver ion, $\overset{+}{\mathrm{A}}\mathrm{g}$,** precipitates white, curdy silver cyanate, AgOCN, which, like silver cyanid, is soluble in ammonium hydroxid. Unlike silver cyanid, it is also soluble in dilute nitric acid.

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* Commercial potassium cyanid usually contains potassium cyanate.

Thiocyanic or Sulfocyanic Acid, HSCN.

Thiocyanic acid is readily formed by the action of sulfur on the cyanids of the alkali metals (see page 126). It is a volatile liquid, B. P. 85°, in general closely analogous to cyanic acid, but is much less readily decomposed by water. Its salts are more stable. The thiocyanates of the alkalies fuse unchanged out of contact with air, showing various colors, yellow, green, blue, as the temperature rises. On cooling they become white again. Thiocyanates of the heavy metals decompose on fusion into sulfates. Mercurous thiocyanate swells up tremendously on heating. Advantage is taken of this property in making the "Pharoah's serpents" frequently found among pyrotechnics.

Both **the acid and its salts** are readily oxidized. Heated in the air, thiocyanates are converted in cyanates and sulfates.

$$\mathbf{KSCN} + 2O_2 + H_2O \rightarrow \mathbf{KHSO_4} + HOCN$$

The same reaction takes place in alkaline solution but, in the presence of acid, sulfuric and hydrocyanic acids are the usual products.

In **HSCN** three acid-forming elements are united together. This combination results in the production of one of the strongest known acids. In solution, it is dissociated quite as completely as hydrochloric or nitric acids.

Thiocyanates are generally soluble, with the exception of the salts of silver, lead, mercury and copper, all of which are transposed on boiling with sodium carbonate.

The **common ion** is **$\overset{-}{SCN}$,** although complex ions are known.

The **barium ion, $\overset{++}{Ba}$,** gives no precipitate.

The **silver ion, $\overset{+}{Ag}$,** precipitates silver thiocyanate, AgSCN, a white, curdy precipitate, soluble in ammonium hydroxid but not in nitric acid. It is readily soluble in an excess of an alkaline thiocyanate, forming a complex salt.

The **ferric ion, $\overset{+++}{Fe}$,** produces a deep red color in dilute hydrochloric acid solutions, due to the formation of ferric thiocyanate, $Fe(SCN)_3$. The color becomes more intense in the presence of an excess of either salt. On addition of mercuric chlorid, the color vanishes, due to the formation of a colorless complex mercury salt of thiocyanic and hydrochloric acids.

$$2Fe(SCN)_3 + 6HgCl_2 \rightarrow 2FeCl_3 + 3(Hg(SCN)_2.HgCl_2)$$

Ferrocyanic Acid, $\mathbf{H_4(Fe=C_6N_6)}$.

Ferrocyanic acid is a white crystalline solid acting as a fairly strong tetrabasic acid, readily soluble in water, oxidizing and decomposing slowly in solution on exposure to air. All of its salts are more stable than the free acid. The alkali and the alkaline earth metals form readily soluble salts, the solutions of which react neutral to litmus. Salts of other metals are generally highly insoluble and do not dissolve in cold dilute mineral acids. At the boiling temperature, dilute sulfuric acid of fair concentration slowly decomposes them with the liberation of hydrocyanic acid. Hot concentrated sulfuric acid breaks down all ferrocyanids and sets free carbon monoxid, according to the equation:

$$\mathrm{K_4(Fe=C_6N_6) + 6H_2SO_4 + 6H_2O \rightarrow}$$
$$\mathrm{FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4 + 6}\mathit{CO}$$

Some ferrocyanids are not readily transposed by boiling with sodium carbonate and require the stronger action of the caustic alkalies.

$$\mathbf{Fe_2(Fe=C_6N_6)} + \mathrm{4KOH \rightarrow K_4(Fe=C_6N_6)} + \mathbf{2Fe(OH)_2}$$

On ignition all are decomposed into the simple cyanids which then act individually. (See page 126.)

Ferrocyanids *are compounds of ferrous iron,* the ion, $(\mathrm{Fe}=\overset{=}{\mathrm{C}}_6\mathrm{N}_6)$, containing an atom of the metal in the divalent condition. Ferrous iron tends to pass into the ferric condition, in complex ions only a little less readily than when existing as simple ions. Hence ferrocyanids are mild reducing agents which, in acid solutions, tend to absorb oxygen and become ferricyanids or compounds of ferric iron.

$$\mathrm{2K_4(Fe=C_6N_6)} + \mathit{O} + \mathrm{H_2SO_4 \rightarrow 2K_3(Fe \equiv C_6N_6) + K_2SO_4 + H_2O}$$

or writing an ionic equation,

$$2(\mathrm{Fe}=\overset{=}{\mathrm{C}}_6\mathrm{N}_6) + \mathit{O} + \overset{+}{\mathrm{H}} \rightarrow 2(\mathrm{Fe} \equiv \overset{=}{\mathrm{C}}_6\mathrm{N}_6) + 2\overset{+}{\mathrm{K}} + \mathrm{H_2O}$$

The **ferrocyanid ion, $(\mathbf{Fe}=\overset{=}{\mathbf{C}}_6\mathbf{N}_6)$,** is one of the most stable of all complex ions. Even at a great dilution there is no appreciable decomposition into the simple ions. The presence of $\overset{+}{\mathrm{H}}$ ions, which is sufficient to decompose most other complex ions, is without noticeable effect at ordinary temperatures and as indicated, it requires the boiling temperature to cause decomposition which takes place according to the following reaction:

$$(\mathrm{Fe}=\overset{=}{\mathrm{C}}_6\mathrm{N}_6) \rightarrow 6\bar{\mathrm{C}}\mathrm{N} + \overset{++}{\mathrm{Fe}}$$

In acid solutions the ferrocyanid ion passes over into the ferricyanid ion under the influence of oxidizing agents, as previously noted.

The **barium ion, $\overset{++}{Ba}$,** with the ferrocyanid ion gives no precipitate.

The **silver ion, $\overset{+}{Ag}$,** precipitates white $Ag_4(Fe=C_6N_6)$, insoluble in dilute nitric acid and ammonium hydroxid.

When the **ferrous ion, $\overset{++}{Fe}$,** is added to a solution containing the ferrocyanid ion, $(Fe=\overline{C}_6N_6)$, out of contact with the air, a white precipitate of potassium ferrous ferrocyanid, $K_2Fe(Fe=C_6N_6)$, or ferrous ferrocyanid, $Fe_2(Fe=C_6N_6)$, forms. The ferrous ion is so easily oxidized that, under ordinary conditions, these precipitates are of a light blue color, due to the formation of a small amount of ferric salt.

The **ferric ion, $\overset{+++}{Fe}$,** precipitates ferric ferrocyanid, "Prussian blue," $Fe_4(Fe=C_6N_6)_3$. (See page 226.)

Ferricyanic Acid, $H_3(Fe \equiv C_6N_6)$.

Ferricyanic acid is a tribasic acid similar in character to ferrocyanic acid, but less stable. Its alkali, alkaline earth and ferric salts are soluble in water; others are insoluble in water and in cold dilute acids. Heated alone or with sulfuric acid the decomposition is the same as that of the ferrocyanids. Ferricyanids are transposed by boiling with sodium carbonate; in certain cases better with sodium hydroxid.

Ferricyanids *are compounds of ferric iron* which, in the presence of reducing agents, tends to pass into the ferrous condition and form ferrocyanids. This reaction takes place better in alkaline than in acid solution.

$$2K_3(Fe \equiv C_6N_6) + 2KOH + 2H— \rightarrow 2K_4(Fe=C_6N_6) + 2H_2O$$

or writing an ionic equation,

$$2(Fe \equiv \overline{C}_6N_6) + 2\ \overline{O}H + 2H— \rightarrow 2(Fe=\overline{C}_6N_6) + 2H_2O$$

The **ferricyanid ion, $(Fe \equiv \overline{C}_6N_6)$,** is far more stable than complex ions generally, but it decomposes more readily than the ferrocyanid ion, $(Fe=\overline{C}_6N_6)$. (See page 13.)

The **barium ion, $\overset{++}{Ba}$,** gives no precipitate.

The **silver ion, $\overset{+}{Ag}$,** precipitates orange silver ferricyanid, $Ag_3(Fe \equiv C_6N_6)$, insoluble in nitric acid, but soluble in ammonium hydroxid.

The **ferrous ion, $\overset{++}{Fe}$,** precipitates dark blue ferrous ferricyanid, Turnbull's blue, $Fe_3(Fe \equiv C_6N_6)_2$. It does not dissolve in acids, but is soluble in alkalies, being transposed according to the equation:

$$\mathbf{Fe_3(Fe \equiv C_6N_6)_2} + 6NaOH \rightarrow \mathbf{3Fe(OH)_2} + 2Na_3(Fe \equiv C_6N_6)$$

The products of this metathesis interact, however, the ferricyanid breaking down into ferrocyanid and oxidizing ferrous to ferric hydroxid.

The **ferric ion, $\overset{+++}{\mathbf{Fe}}$,** gives a brownish-green or yellow color according to the dilution of the solution.

SILICON. Si — 28.4.

Elementary silicon is known in two modifications which suggest the similar forms of carbon. Amorphous silicon is a soft brown powder which melts at a high temperature and then solidifies to a hard black mass of brilliant crystals which are much more resistant than the amorphous form. Neither modification is active at ordinary temperatures, but each generally requires high heating to make it enter into combination with other elements. Heated in the air, silicon burns to the dioxid, SiO_2. Acids are without effect, with the exception of hydrofluoric acid in which silicon dissolves readily, thus showing some slight indication of metallic properties.

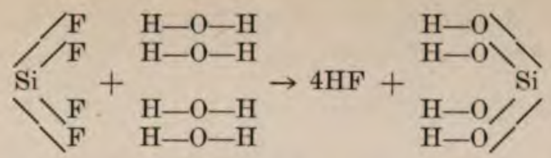
$$\mathbf{Si} + 4HF \rightarrow SiF_4 + 2H_2$$

Silicon fluorid, as well as other halogen compounds, is decomposed by water, however, thus indicating that silicon is acidic rather than metallic in nature. This fact is further evidenced by the formation of silicon acids and of silicids of the metals. These bodies, like the hydrids, of which several are known, are in general analogous to the corresponding compounds of carbon. In all its compounds, silicon acts as a tetravalent element.

Silicon fluorid, SiF_4, is a heavy, colorless gas with a very pungent, stifling odor. It unites with hydrogen fluorid to form hydrosilicofluoric acid (see page 136) according to the equation:

$$SiF_4 + 2HF \rightarrow H_2SiF_6$$

Silicon fluorid is decomposed by water into hydrofluoric and silicic acids, as indicated in the following equation, but some of the unchanged SiF_4 reacts with HF produced during the reaction to form some H_2SiF_6.



Silicon dioxid, silica, SiO_2, exists in at least three different modifications, one amorphous and two crystalline. The naturally-occurring crystalline form, quartz, is the best known, "rock crystal" being the pure substance. Small amounts of different impurities give rise to many different varieties which are known as rose, yellow, smoky and black quartz, topaz, onyx and amethyst. White sand consists almost entirely of finely broken quartz. All these forms are exceedingly hard, insoluble and resistant to chemical agents (except hydrofluoric acid) and fuse only at the temperature of the oxyhydrogen blow pipe, *i. e.,* about 1800°–2000°.

Tridymite is the second modification, possessing a different crystalline form from quartz, but otherwise resembling it closely. It occurs as a rock constituent.

Amorphous silica occurs as chalcedony, agate and flint. These naturally-occurring forms do not differ much from quartz, but as obtained artificially, silica is more soluble and readily attacked by chemical reagents than the crystalline form. With hydrofluoric acid, all compounds of silicon react more readily than with any other common reagent. All forms of silica dissolve readily, forming silicon fluorid and water.

Silicon dioxid is the anhydrid of silicic acid, from which it is readily formed by heating. More than one-quarter of the known crust of the earth is silicon, existing combined as the anhydrid or as salts of silicic acid.

Silicic Acid.

Ortho-silicic acid, H_4SiO_4, is exceedingly unstable under ordinary conditions. It may lose water in many different proportions. From one molecule of acid, one molecule of water separates, forming **meta-silicic acid, H_2SiO_3.** From two molecules of H_4SiO_4, by the loss of one, two and three molecules respectively of water, $H_6Si_2O_7$, $H_4Si_2O_6$, and $H_2Si_2O_5$, are derived, while from three molecules of H_4SiO_4, by separation of water, other partially-dehydrated acids are formed as shown in the accompanying equations:

(1) $2H_4SiO_4 - H_2O \rightarrow H_6Si_2O_7$
(2) " $- 2H_2O \rightarrow H_4Si_2O_6$
(3) " $- 3H_2O \rightarrow H_2Si_2O_5$
(4) $3H_4SiO_4 - H_2O \rightarrow H_{10}Si_3O_{11}$
(5) $3H_4SiO_4 - 2H_2O \rightarrow H_8Si_3O_{10}$
(6) " $- 3H_2O \rightarrow H_6Si_3O_9$
(7) " $- 4H_2O \rightarrow H_4Si_3O_8$
(8) " $- 5H_2O \rightarrow H_2Si_3O_7$

These compounds are known as **polysilicic acids,** numbers (2) and (6) obviously having the same proportionate composition as meta-silicic acid. Whether all of these acids have an existence even in solution is very questionable, since no methods of differentiating them are known. The water content of silicic acid seems to depend only on the temperature to which it is heated, nothing definite being obtained except the completely dehydrated SiO_2.

The solubility of the acid seems to correspond in a general way with the state of hydration, the more highly-hydrated forms being the most soluble. In acids it is somewhat more soluble than in pure water, while solutions of the fixed alkalies, both carbonates and hydroxids, have a very decided solvent action even on the very resistant quartz, when it is finely powdered. Most of the solutions possess the properties of pseudo-solutions quite as much as of true solutions.

Although the anhydrid, SiO_2, is not formed completely below a red heat, a temperature of 110–130° produces sufficient dehydration to give a product insoluble in water and dilute acids. This drying-out process, known as *desiccation,* is frequently used as a means for the separation of silicic acid from solution.

Silicic acid dissociates so little that its aqueous solutions give no evidence of the presence of $\overset{+}{H}$ ions when tested with red litmus. Silicate ions are, therefore, practically unknown. Soluble silicates undoubtedly ionize, but hydrolysis takes place to such an extent as to remove the silicate ions almost entirely from solution as free silicic acid. Insoluble silicates may be precipitated from solutions of soluble silicates on the addition of certain metallic ions, it is true, yet the concentration of silicate ions actually existing in solution at any given moment must be very small indeed. None of the reactions by which silicic acid is separated and detected are typical ionic reactions.

Salts of silicic acid, both simple silicates and polysilicates, are well-known, many being the common rock-forming minerals. They are among the most stable substances at high temperatures. The simpler silicates are generally of the type derived from meta-silicic acid, H_2SiO_3. With the exception of the silicates of the alkali metals, all are highly insoluble, many of them being so little soluble that they are not affected by the ordinary *strong* acids, contrary to the general rule for salts of weak acids.

Soluble silicates of sodium and potassium are known as "water glass." These solutions are hydrolyzed to a very great degree and react strongly alkaline.

Ammonium silicate is unknown, for it cannot be formed in the "dry way" and attempts to produce it in the "wet way" result only in a completely hydrolyzed product. To illustrate: When a solution of an alkaline silicate is treated with the ammonium salt of a strong acid, such as NH_4Cl, there is evidence that a metathesis occurs to form an alkaline chlorid and ammonium silicate. This latter compound hydrolyzes and the silicic acid is nearly all precipitated from a warm solution, especially on standing. If ammonium carbonate is substituted for ammonium chlorid, the precipitation is not complete, since sodium carbonate is a solvent for silicic acid. Ammonium hydroxid gives no precipitate under these conditions.

Many **silicates** are decomposed by acids and, on evaporation of the solution, the silicic acid separates in the form of a jelly, which, at 120°, loses most of its water, leaving an insoluble residue like powdered glass.

Most silicates, insoluble in acids, are not transposed by boiling with sodium carbonate. They may be decomposed by fusing with the dry reagent, however, forming sodium silicate and oxids of the metals, which then readily dissolve in acids. Fusion with ammonium carbonate will not decompose silicates in this way. If, however, a finely powdered silicate, intimately mixed with twice its weight of ammonium chlorid and four times as much calcium carbonate, be heated, decomposition occurs probably due to the more energetic action of ammonium carbonate freshly formed by the interaction of NH_4Cl and $CaCO_3$. This method is sometimes necessary in decomposing natural silicates which are to be tested for alkali metals.

All silicates whatsoever are decomposed by hydrofluoric acid, forming volatile silicon fluorid, which may be driven off by heat.

$$\mathbf{CaSiO_3} + 6HF \rightarrow \mathbf{CaF_2} + SiF_4 + 3H_2O$$

Since silicon fluorid is decomposed by water into hydrofluoric and silicic acids (see page 133), in order to remove the silica entirely by volatilization, the water set free in the reaction must be removed. This is most satisfactorily accomplished by concentrated sulfuric acid. Since glass is essentially a mixture of silicates, all reactions with hydrofluoric acid must be performed in platinum vessels. (See page 199.)

Silica, being an acid anhydrid, will not unite with fused sodium meta-phosphate, and therefore remains as an insoluble, unfused residue floating about in the hot bead. Most silicates are decomposed by fusion with sodium meta-phosphate, the metallic oxid uniting with the phosphate and dissolving in the bead, leaving the "skeleton" of SiO_2. A few silicates are not thus decomposed, and can not be detected by this reaction, since they fuse and mix with the bead without leaving a visible residue.

Hydrosilicofluoric Acid, $\mathbf{H_2SiF_6}$.

Silicon fluorid unites with hydrofluoric acid to form a complex body according to the equation:

$$SiF_4 + 2HF \rightarrow H_2SiF_6$$

This compound, H_2SiF_6, is known as **hydrosilicofluoric** or **hydrofluosilicic acid.** The reaction by which it is formed proceeds most satisfactorily in concentrated solutions of hydrofluoric acid. Since silicon fluorid reacts with water to form hydrofluoric acid (and silicic acid), hydrosilicofluoric acid also is formed. The following equation is often written to express this reaction, but it is hardly probable that it shows the true way in which hydrosilicofluoric acid is formed:

$$3SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + \mathbf{H_2SiO_3}$$

Hydrosilicofluoric acid is about as strong as sulfuric or dichromic acid. It is known only in solution, for, on every attempt to isolate it, it decomposes into silicon fluorid and hydrofluoric acid.

All silicofluorids are readily soluble in water with the exceptions of the salts of the alkali metals and of barium. Na_2SiF_6 is soluble in about 150 parts of H_2O, K_2SiF_6 in about 825 parts, and $BaSiF_6$ in about 3500 parts at ordinary temperatures.

All silicofluorids are decomposed in alkaline solution into salts of silicic and hydrofluoric acids, according to the equation:

$$Na_2SiF_6 + 6NaOH \rightarrow 6NaF + Na_2SiO_3 + 3H_2O$$

Ammonium hydroxid precipitates silicic acid because of hydrolysis of the ammonium silicate. (See page 135.)

All silicofluorids are decomposed on heating into fluorids of silicon and of the metal. Concentrated sulfuric acid forms sulfates and liberates silicon fluorid and hydrofluoric acid.

The **silicifluorid ion** is $\mathbf{Si\overline{F}_6}$.

The **barium ion, $\overset{++}{\mathrm{Ba}}$,** precipitates white crystalline $BaSiF_6$ which is somewhat soluble in HCl. (See page 100.)

The **silver ion, $\overset{+}{\mathrm{Ag}}$,** gives no precipitate.

Group 4, Second Type.

Germanium 72.5; **Tin 119; Lead 206.9.**

The elements of this type closely resemble those of the first type, but are rather more metallic in properties, being soft, lustrous, heavy, easily-fusible metals. The hydroxids ordinarily act as weak bases, but, under proper conditions, may show acid properties. The valence of the element is quite as often two as four. The metals do not pass readily into the ionic conditions, hence they may be obtained from their compounds without difficulty.

Germanium is of rare occurrence and will not be treated further.

TIN (Stannum). Sn — 119.

Tin is a rather soft, silver-white metal, under ordinary conditions possessing a crystalline structure. It does not tarnish in the air at ordinary temperatures. When heated, it oxidizes slowly until a white heat is reached, when it burns rapidly to the white oxid, SnO_2.

The **metal** dissolves slowly in fairly dilute solutions of the strong mineral acids, forming in every instance stannous compounds in which the metal is bivalent. In hot concentrated acids the action often differs from that in dilute solutions. Hydrochloric acid forms stannous chlorid, $SnCl_2$, but sulfuric acid produces the tetravalent stannic sulfate, $Sn(SO_4)_2$, together with SO_2, S and H_2O.

Fairly concentrated HNO_3 doubtless oxidizes the stannous nitrate, first formed, over to stannic nitrate. Tetravalent tin salts are weaker than the bivalent compounds and hydrolyze very considerably. In the present instance stannic hydroxid, $Sn(OH)_4$, is formed. This loses a molecule of water and becomes $SnO(OH)_2$, several molecules of which unite to form a compound molecule, $(SnO(OH)_2)_x$, where x possibly equals five. Stannic hydroxid possesses acidic as well as basic properties, hence it is often called stannic acid. The highly insoluble compound formed by the action of concentrated HNO_3 on tin is known as β stannic acid to distinguish it from the ordinary soluble form.

Tin is quite indifferent to the passage into the ionic condition, no considerable amount (if any) of energy being absorbed or liberated during the reaction. For this reason, several metals showing a greater tendency to pass into the ionic condition, especially zinc, magnesium and aluminum, will precipitate metallic tin from solutions of its salts. On the other hand, silver, mercury, bismuth, copper, platinum and gold are thrown out of solutions of their salts when metallic tin is introduced.

Stannous compounds show a very strong tendency to become tetravalent and will react with most oxidizing agents and pass into the stannic condition. For this reason stannous chlorid, $SnCl_2$, is one of the most satisfactory reducing agents for general laboratory use. By it, mercuric salts are changed first into the mercurous condition and finally into the metal. Compounds of arsenic in both stages of oxidation are reduced to the element (Bettendorf Test for arsenic). Ferric salts are reduced to the ferrous condition and the highly oxidized acidic compounds of chromium and manganese are reduced to the basic condition.

Stannic compounds, on the other hand, are reduced only with great difficulty, nascent hydrogen being the only agent capable of breaking down stannic salts in solution into the lower condition.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all tin compounds are reduced to the metal. The reaction may be accomplished most readily by adding finely powdered charcoal to the mixture of the tin compound and Na_2CO_3. Even under these conditions long and steady blow-piping is sometimes necessary to obtain the bright, white metallic globule which, as soon as the flame is removed, becomes covered with a coating of white oxid. The globule is malleable (distinction from Sb and Bi). It does not dissolve in HNO_3, but is changed to a white powder (like Sb but different from Pb and Ag). The globule is readily soluble in HCl. A white coating of the oxid is formed on the charcoal.

The **compounds of tin** in both stages of oxidation are generally colorless. Salts of the common strong mineral acids are usually soluble but since tin is but a weak base-forming element, they tend to hydrolyze. Hence a little acid must be added to the solutions of tin salts to prevent the formation of insoluble basic salts.

Of the **tin ions,** the stannous ion, $\overset{++}{\mathrm{Sn}}$, is well known. Although the stannic ion, $\overset{++++}{\mathrm{Sn}}$, is recognized, its compounds dissociate but little and in solution the tin exists for the most part as pseudo-solutions of stannic hydroxid. Tin enters into several anions of which the stannite ion, $\mathrm{S\bar{n}O_2}$, the stannate ion, $\mathrm{S\bar{n}O_3}$, and the thiostannate ion, $\mathrm{S\bar{n}S_3}$, are the most important.

Since the compounds of the Sn ion are quite different from the compounds of the $\overset{++++}{\mathrm{Sn}}$ ion in their properties, they will be considered separately. Solutions of the chlorids serve satisfactorily for the reactions of each ion.

The Stannous Ion, $\overset{++}{\mathbf{Sn}}$.

The **hydroxyl ion, $\overset{-}{\mathbf{OH}}$,** added to a solution containing the $\overset{++}{Sn}$ ion, precipitates white $Sn(OH)_2$ which loses water on heating and breaks down into the black SnO. Stannous oxid unites with oxygen so readily, however, that it will take fire and burn to white stannic oxid, SnO_2.

In the bivalent **stannous hydroxid,** basic properties are more strongly developed than acid properties. The latter are sufficiently strong, however, to cause the hydroxid to dissolve in solutions of the strong alkalies, NaOH and KOH, but when the concentration of $\overset{-}{OH}$ ions is much less as in solutions of NH_4OH and in alkaline carbonates, stannous hydroxid is not appreciably soluble. But few salts of stannous acid, H_2SnO_2, are definitely known, and aside from Na_2SnO_2 and K_2SnO_2 they are of little importance. Solutions of these salts are very strongly hydrolyzed. This action increases so much as the temperature is raised that a brown-black precipitate of SnO is formed. The reactions producing this body are simply hydrolysis and dehydration, as shown by the equations:

$$Na_2SnO_2 + 2H_2O \rightarrow \mathbf{Sn(OH)_2} + 2NaOH$$
$$\mathbf{Sn(OH)_2} \rightarrow \mathbf{SnO} + H_2O$$

Like all bivalent tin compounds, alkaline stannites are very strong reducing agents. When heated, especially if KOH or NaOH be present in excess, one portion of the stannite is oxidized to stannate at the expense of the other, which is reduced to the metal and precipitated as a black powder.

$$2Na_2SnO_2 + H_2O \rightarrow Na_2SnO_3 + \mathbf{Sn} + 2NaOH$$

The reducing action of alkaline stannites is used in testing for bismuth salts. (See page 171.)

The **carbonate ion, $\overset{=}{\mathbf{CO}}_3$,** has no specific effect, as stannous carbonate is unknown. Alkaline carbonate solutions act like very weak hydroxid solutions, precipitating $Sn(OH)_2$.

The **sulfid ion, $\overset{=}{\mathbf{S}}$,** precipitates dark brown stannous sulfid from acid solutions only. The concentration of $\overset{+}{H}$ ions is not too great, for SnS is readily soluble in strong HCl. Alkaline polysulfids, because of their excess of sulfur, oxidize SnS over to SnS_2, which then dissolves readily, forming alkaline thiostannates. In monosulfids, SnS is not appreciably soluble and apparently thiostannites do not exist. Stannous sulfid dissolves in strong alkalies with the absorption of oxygen, forming a mixture of stannites and thiostannates.

The **sulfate ion, $\overset{=}{SO}_4$**, produces no precipitate, since $SnSO_4$ is soluble.

The **chlorid ion, $\overset{-}{Cl}$**, produces no precipitate since stannous chlorid is soluble in about one-third its weight of water. It crystallizes according to the formula $SnCl_2.2H_2O$. Being by far the most important compound, it is known commercially as "tin salt." In solution it tends to precipitate a white insoluble basic salt, $Sn<\begin{matrix}OH\\Cl\end{matrix}$, because of hydrolysis; hence a little HCl must be added in order to keep the solution clear. In order to prevent oxidation by the air to $SnCl_4$, it is necessary to keep metallic tin in the solution. This, reacting slowly with the acid, generates nescent hydrogen and preserves the tin in the lower form.

The **iodid ion, $\overset{-}{I}$**, precipitates orange-brown SnI_2, which separates in gleaming spangles. It is quite soluble in water, hence is not precipitated from dilute solutions. It dissolves in an excess of the precipitant, forming a double iodid.

The **cyanid ion, $\overset{-}{CN}$**, forms probably stannous cyanid, but this is completely hydrolyzed and stannous hydroxid is precipitated.

The **phosphate ion, $\overset{\equiv}{PO}_4$**, causes the precipitation of a white oxyphosphate, of varying composition, depending upon the conditions of the experiment and more or less closely approximating the proportions indicated by the formula $Sn_3(PO_4)_2$. It is soluble in strong acids, and in strong alkalies forming alkaline stannites and phosphates.

The Stannic Ion, $\overset{++++}{Sn}$.

The **hydroxyl ion, $\overset{-}{OH}$**, added to solutions containing the $\overset{++++}{Sn}$ ion, probably forms $Sn(OH)_4$ at first, but this loses water and white $SnO(OH)_2$ is precipitated. On heating, white SnO_2 is formed. Tin dioxid is more resistant to the odinary chemical reagents than most substances of frequent occurrence. Neither acids nor aqua regia, nor fusion with alkaline hydroxids or carbonates serve to convert it entirely into a soluble product. By fusing with a mixture of sulfur and alkaline hydroxid or carbonate, stannic oxid is changed into soluble thiostannates, however.

Stannic hydroxid possesses less basic properties than stannous hydroxid but correspondingly stronger acid properties. It dissolves in acids to form stannic salts and in the strong alkalies to form alkaline stannates, which form the ion $\overset{=}{SnO}_3$. Since it is rather acidic than basic, H_2SnO_3 is frequently called stannic acid. Its formula shows that it is of the same type as the more unstable carbonic acid, H_2CO_3. The fact that *stannic* acid anhydrid, SnO_2, is a very resistant solid while carbonic acid anhydrid, CO_2, is volatile, doubtless accounts to a great degreee for the difference in stability between the two acids and their salts. The compound precipitated from solutions of stannic salts by the hydroxyl ion seems to have a single molecule, H_2SnO_3, and is far more soluble and reactive than the polymeric compound formed by the action of fairly concentrated HNO_3 on the metal. The former is known as α stannic acid to distinguish it from the latter compound.

The **carbonate ion,** $\overline{\overline{\mathbf{CO}}}_3$, has no specific action. Solutions of alkaline carbonates precipitate H_2SnO_3 because of their hydrolysis.

The **sulfid ion,** $\overline{\overline{\mathbf{S}}}$, precipitates yellow stannic sulfid, SnS_2, from acid solutions only. The concentration of $\overset{+}{H}$ ions must not be too great, however, for SnS_2 is readily soluble in fairly concentrated HCl. In the strong alkalies, alkaline sulfids and polysulfids, it is soluble, forming thiostannates. In NH_4OH and $(NH_4)_2CO_3$, it is insoluble even when heated (distinction from As).

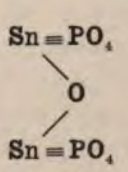
The **sulfate ion,** $\overline{\overline{\mathbf{SO}}}_4$, causes no precipitate, as $Sn(SO_4)_2.2H_2O$ is soluble in water containing sufficient acid to prevent hydrolysis.

The **chlorid ion,** $\overline{\mathbf{Cl}}$, produces no precipitate, as $SnCl_4$ is very soluble. The solutions hydrolyze considerably and, on standing, precipitate white basic salts. On boiling a dilute $SnCl_4$ solution, complete hydrolysis and dehydration of the resulting stannic hydroxid takes place and stannic oxid is precipitated.

The other halids are similar to the chlorid.

The **cyanid ion,** $\overline{\mathbf{CN}}$, precipitates stannic hydroxid.

The **phosphate ion,** $\overline{\overline{\overline{\mathbf{PO}}}}_4$, precipitates white stannic oxyphosphate, which is soluble in the strong acids and alkalies. A formula for this compound may be written:



Thiostannates bear the same relation to stannates that thioarsenates and thioantimonates do to arsenates and antimonates (see pages 164 and 169). Although thioarsenites and thioantimonites are well known, the corresponding thiostannites do not seem to exist. The methods of formation of all salts of thioacids are in general alike. Thiostannates are produced by the action of alkaline polysulfids on SnS, and by alkalies and alkaline sulfids on SnS_2, as indicated by the equations:

$$\mathbf{SnS} + (NH_4)_2S.xS \rightarrow (NH_4)_2SnS_3 + (x-1)S$$
$$\mathbf{3SnS_2} + 6KOH \rightarrow 2K_2SnS_3 + K_2SnO_3 + 3H_2O$$
$$\mathbf{SnS_2} + (NH_4)_2S \rightarrow (NH_4)_2SnS_3$$

Aside from the alkaline thiostannates, few salts are known. The acid is not known with certainty, for it is very unstable and breaks down into H_2S and SnS analogously to the corresponding thioarsenic and thioantimonic acids. Consequently, on acidifying a solution of a thiostannate, yellow SnS_2 is precipitated.

LEAD (Plumbum). Pb — 206.9.

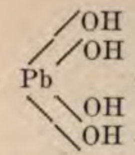
Lead is a heavy, blue-gray metal with considerable lustre, quickly tarnishing in the air because of the formation of a thin film of Pb_2O, a lower oxid of little relative importance. At a higher temperature this compound, as well as the metal, is changed into PbO or litharge.

The metal is but little acted upon by cold dilute HCl or H_2SO_4, owing to the formation of a layer of insoluble chlorid or sulfate. In hot HCl or concentrated H_2SO_4 it dissolves, however, since the protective coatings are soluble under these conditions. Nitric acid and acetic acid are ready solvents for the metal, forming the only common soluble salts. Lead compounds are generally quite insoluble and are, for the most part, colorless.

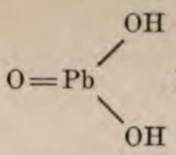
Lead is indifferent toward the passage from the metallic into the ionic state. No considerable amount of energy is either liberated or absorbed when the metal becomes the ion or when the reverse process takes place. Metallic magnesium, zinc and iron, because of their strong tendency to become ionic, will precipitate metallic lead from solutions of its salts, but metallic lead will precipitate mercury, silver, gold and platinum.

On heating before the **blowpipe** with Na_2CO_3 on charcoal, all lead salts are reduced to the metal, forming a bright, malleable (difference from Sb and Bi) globule with a yellow coating on the charcoal (difference from Sn, Ag and Bi). It dissolves readily in HNO_3 (difference from Sn) and gives a precipitate with HCl only in cold, fairly concentrated solutions (difference from Ag).

From the **two typical oxids, PbO** and **PbO_2**, two different series of compounds are formed. In the divalent condition lead is generally basic and from the hydroxid, $Pb(OH)_2$, all the common salts are derived. Tetravalent lead is almost entirely acidic in its properties. The tetravalent hydroxid is a weak acid, of which two forms are known:

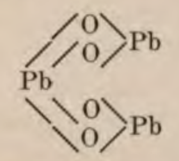


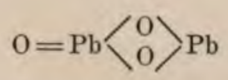
Ortho-plumbic acid.



Meta-plumbic acid.

Well-characterized salts of these acids are known, among which the oxids, Pb_3O_4 and Pb_2O_3, are to be included. Minium, or "red lead," is to be regarded as the lead salt of ortho-plumbic acid, while Pb_2O_3 is the lead salt of meta-plumbic acid. This is indicated by the fact that when Pb_3O_4 is treated with dilute HNO_3, two-thirds of the lead dissolves while one-third remains as insoluble PbO_2, the anhydrid of ortho-plumbic acid. (See also page 214.)





The tetravalent salts of lead are of little relative importance in qualitative analysis.

The **common ion is $\overset{++}{\mathbf{Pb}}$.** Lead is a constituent of some anions of which $P\bar{b}O_2$ is the best known.

For reactions of the $\overset{++}{Pb}$ ion, solutions of the nitrate or acetate are very satisfactory. The nitrate, $Pb(NO_3)_2$, dissolves in about two parts of water and separates from solution without water of crystallization. "Sugar of lead," $Pb(C_2H_3O_2)_2.3H_2O$, is about as soluble but, on exposure to the air, becomes turbid owing to the formation of a white basic carbonate, due to the action of the carbon dioxid present in the atmosphere.

The **hydroxyl ion, $\overset{-}{\mathbf{OH}}$,** precipitates from solutions containing the $\overset{++}{Pb}$ ion white, floccy $Pb(OH)_2$. After being washed free from all of the reagent used to precipitate it, lead hydroxid gives a slight basic reaction to litmus, thus showing it to be somewhat soluble (8,000 parts H_2O) and to separate $\overset{-}{OH}$ ions to a slight degree.

Lead hydroxid is also capable of separating $\overset{+}{H}$ ions and of acting as a very weak acid. A high concentration of hydroxyl ions, such as is given by the strong alkaline hydroxids, is necessary to cause this change in character. When NaOH is added to a solution containing PbO_2H_2 in suspension, the readily-dissociating strong base represses the ionization of lead hydroxid as a base (see page 31). The concentration of $\overset{++}{Pb}$ ions is thereby lessened and PbO_2H_2 passes into solution (see page

36). On the other hand, the tendency for lead hydroxid to separate $\overset{+}{\mathrm{H}}$ and $\mathrm{P\overline{b}O_2}$ ions is stimulated, owing to the fact that the $\overline{\mathrm{OH}}$ ions from the alkali unite with the $\overset{+}{\mathrm{H}}$ ions from the $\mathrm{PbO_2H_2}$ to form undissociated water. The only lead-containing ion left in solution by these reactions is the plumbite ion, $\mathrm{P\overline{b}O_2}$, together with an abundance of ions of the alkali metal to form, on evaporation of the solution, an alkaline plumbite. Thus, $\mathrm{PbO_2H_2}$ may be either the base—lead hydroxid—or plumbous acid.

In the presence of $\mathrm{NH_4OH}$, lead hydroxid is insoluble, since the former is not sufficiently strong to make the latter act as plumbus acid.

With the exception of a few very highly insoluble compounds, all lead salts are appreciably soluble in the strong alkaline hydroxids.

The **carbonate ion, $\overline{\mathrm{CO}}_3$**, precipitates white $\mathrm{PbCO_3}$. As ordinarily brought down by alkaline carbonates, however, the precipitate consists partly of $\mathrm{Pb(OH)_2}$. Because of the hydrolysis of the precipitants, their solutions contain the $\overline{\mathrm{OH}}$ ion as well as the $\overline{\mathrm{CO}}_3$ ion. Since $\mathrm{PbCO_3}$ and $\mathrm{Pb(OH)_2}$ are about equally soluble, a mixture of these two salts falls. Whether this precipitate, the "white lead" of commerce, is really a mixture or a true basic salt (see page 21) is not yet definitely proven.

The **sulfid ion, $\overline{\mathrm{S}}$**, precipitates black PbS from both alkaline and acid solutions. From fairly acid solutions, especially in the presence of HCl, $\mathrm{H_2S}$ precipitates a red complex salt having the proportions represented by the formula $\mathrm{PbS.PbCl_2}$. On further treatment with $\mathrm{H_2S}$, the normal sulfid is formed. Lead sulfid is soluble in strong HCl and in hot, dilute $\mathrm{HNO_3}$, since the boiling reagent oxidizes it to free sulfur (or $\mathrm{H_2SO_4}$) and $\mathrm{Pb(NO_3)_2}$.

The **sulfate ion, $\overline{\mathrm{SO}}_4$**, causes the precipitation of granular, white $\mathrm{PbSO_4}$ which is soluble in about 23,000 parts of water at ordinary temperatures and somewhat more soluble in dilute solutions of the stronger acids. In concentrated $\mathrm{H_2SO_4}$, it dissolves to a considerable extent, owing to the formation of a soluble acid salt. On dilution, however, the acid salt is decomposed and $\mathrm{PbSO_4}$ again precipitated. Commercial $\mathrm{H_2SO_4}$ always contains some of this salt, since the acid is concentrated in lead pans. Lead sulfate is soluble in NaOH and KOH, forming alkaline plumbites and sulfates both of which are soluble. Furthermore, it dissolves in strong solutions of the ammonium salts of several organic acids, the acetate, tartrate and citrate being most commonly used. The reaction with ammonium acetate appears to be simply a metathesis forming lead acetate. This substance, normally dissociating much less than other salts, has its ionization repressed by the greater dissociation of ammonium acetate. Therefore but few $\overset{++}{Pb}$ ions exist in solution, the concentration being insufficient to precipitate $PbSO_4$ again.

The **chromate ion, $\overset{=}{CrO_4}$**, precipitates yellow $PbCrO_4$, soluble in about 100,000 parts of water at ordinary temperatures and in the strong acids and alkalies as would be expected. (See opposite page.)

The **chlorid ion, $\overset{-}{Cl}$**, precipitates curdy, white $PbCl_2$, soluble in about 100 parts of water at ordinary temperatures and in about 25 parts of boiling pater. For this reason, the $\overset{++}{Pb}$ ion can be removed only partially from solution by the addition of the $\overset{-}{Cl}$ ion.

The **bromid ion, Br**, precipitates pale yellow $PbBr_2$, similar to $PbCl_2$, but less soluble.

The **iodid ion, $\overset{-}{I}$**, brings down yellow PbI_2, similar to the other halids of lead, but less soluble, dissolving in about 1300 parts of water at ordinary temperatures and 194 parts at 212°. On cooling, the salt separates in the form of brilliant spangles. Lead iodid is appreciably soluble in an excess of KI forming a double salt of the formula $PbI_2.2KI$. In strong solutions the ions are $2\overset{+}{K}$ and $\overset{=}{Pb}I_4$, thus showing the formation of a new compound in which the lead is found in the anion. This tendency toward the formation of new ions of this character is noticeable with the bromids and not very appreciable among the chlorids. With the iodids, however, it is well developed in the salts of other metals as well as those of lead. (See similar mercury salts, page 109.)

The **cyanid ion, $\overset{-}{CN}$**, precipitates white $Pb(CN)_2$, insoluble in an excess of alkaline cyanids, but dissolving in acids and strong alkalies.

The **phosphate ion, $\overset{\equiv}{PO_4}$**, brings down floccy white $Pb_3(PO_4)_2$, readily soluble in acids and in strong alkalies.

Group 5, First Type.

Nitrogen 14; Phosphorus 31; Arsenic 75; Antimony 120.2;
Bismuth 208.5.

The members of this group show characteristic valences of three or five. The elements with low atomic weights, nitrogen and phosphorus, are typical non-metals, the pentavalent compounds of which are more stable than the trivalent. The elements of high atomic weights are typically metallic in appearance, being heavy and lustrous. Pentavalent compounds of bismuth and antimony are less stable than the corresponding trivalent compounds, while with arsenic each form possesses approximately equal stability. The hydrids are rather unstable, those of nitrogen and phosphorus uniting with water to form weak bases, while those of arsenic and antimony are neutral in character.

Oxygen unites with these elements readily in various proportions, trioxids and pentoxids being most typical. These unite with water, generally directly, to form hydroxids. The gradation of properties noticed in all groups is especially prominent in this group. Trivalent hydroxids of the elements with low atomic weights are acids, while the corresponding compounds of elements with high atomic weight are bases. All pentavalent hydroxids are acidic in nature, but, while HNO_3 is one of the strongest acids, $HBiO_3$ is very weak.

NITROGEN. N — 14.

Nitrogen is a colorless, tasteless, odorless gas, existing uncombined in the atmosphere, of which it constitutes about four-fifths. It is not appreciably soluble in any solvent. One of its chief characteristics is its inertness. It requires the expenditure of considerable energy to make it unite with other substances. Although its true character is much concealed by its inactivity, nitrogen acts as a typical acid-forming element. The rare hydronitric acid, HN_3, resembles the other acid hydrids. In solution, it dissociates into the ion $\bar{N}_3$ to a much greater degree than H_2S ionizes, but not so much as HF. With certain metals, nitrids are formed—from magnesium, as an illustration, Mg_3N_2—which are decomposed by water, liberating NH_3 and forming the hydroxid of the metal.

$$\mathbf{Mg_3N_2} + 6HOH \rightarrow 3\mathbf{Mg(OH)_2} + 2NH_3$$

These compounds are of scientific importance only. United with hydrogen and oxygen, however, nitrogen forms several important ions. The detection of nitrogen itself comes properly under the subject of gas analysis and will not be considered here.

Nitrogen compounds are of two distinct types. In one the element is trivalent; in the other it shows five valences. The normal tendency is toward the formation of the pentavalent compounds, trivalent compounds being generally less stable than the higher form into which they tend to pass quite readily.

With **hydrogen,** nitrogen forms compounds of a basic nature,* the most important of which is **ammonia, NH_3**. It is a colorless gas with a pungent odor, reacting readily with many substances, generally by direct addition, forming compounds in which the nitrogen becomes pentavalent. It is extremely soluble, one litre of water dissolving nearly 800 volumes of gas at ordinary temperature and pressure, forming a solution which is known as "ammonia water." Part of the dissolved NH_3 unites with the water to form a compound, NH_4OH, which dissociates into $\overset{-}{OH}$ and $\overset{+}{NH_4}$ ions and has a distinct basic reaction. Ammonia unites with especial readiness with many metallic ions forming complex ions of various types, such as $\overset{+}{Ag}.(NH_3)_2$, $\overset{++}{Cu}.(NH_3)_4$ and $\overset{+++}{Co}.(NH_3)_6$ (see also cadmium, chromium, nickel, zinc and mercury). The union of ammonia with water, or ammonia with acids, may be regarded as a similar reaction, *i. e.*, the union of NH_3 with the $\overset{+}{H}$ ion to form the $\overset{+}{NH_4}$ ion, as the equations show:

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* Except hydronitric acid, HN_3.

$$\begin{array}{ll}
NH_3 + H_2O \rightarrow NH_4OH & \qquad NH_3 + HCl \rightarrow NH_4Cl \\
NH_3 + \overset{+}{H} + \overset{-}{OH} \rightarrow \overset{+}{NH_4} + \overset{-}{OH} & \qquad NH_3 + \overset{+}{H} + \overset{-}{Cl} \rightarrow \overset{+}{NH_4} + \overset{-}{Cl} \\
NH_3 + \overset{+}{H} \rightarrow \overset{+}{NH_4} & \qquad NH_3 + \overset{+}{H} \rightarrow \overset{+}{NH_4}
\end{array}$$

Inasmuch as the $\overset{+}{NH_4}$ ion is very stable and unites with the anions of acids to form a whole series of salts in which the univalent radicle, (NH_4), acts as a metal, the radicle is called ammonium, the ending "ium" signifying the possession of metallic properties. Since ammonium salts most closely resemble those of potassium, the former are treated in detail immediately following the consideration of the latter, page 75.

With **oxygen,** nitrogen forms five compounds all of which are more or less acidic in nature.

Nitrogen monoxid, N_2O, is a colorless gas with a sweet taste and odor, somewhat soluble in water. Although it is the anhydrid of the rare hyponitrous acid, $(HNO)_2$, it does not unite with water to form the acid. At ordinary temperatures the gas is quite stable, neither taking on more oxygen nor giving up its own. At a higher temperature, however, it decomposes into its elements and becomes a good oxidizing agent.

Nitrogen dioxid, N_2O_2 (as it is often called and written for the sake of systematization, although the molecule is really NO and contains but one atom of nitrogen and one of oxygen), is a colorless gas not appreciably soluble in water. It parts with its oxygen less readily than any other oxid of nitrogen and, therefore, is the decomposition product formed most frequently when higher oxidized compounds, such as nitrates and nitrites, break down. On exposure to the atmosphere, it readily takes up more oxygen, forming brown N_2O_4. Nitrogen dioxid unites with ferrous salts in concentrated solutions to form a very characteristic dark brown compound, with ferrous sulfate having the composition $(FeSO_4)_2.NO$. It is very unstable, however, and, on warming or diluting, is decomposed and the color disappears. (See pages 149 and 151.)

Nitrogen trioxid, N_2O_3, may be obtained as a blue liquid at low temperatures. At zero or below, it decomposes into a mixture of the dioxid and tetroxid, hence has no existence at ordinary temperatures. It is the anhydrid of nitrous acid, HNO_2.

Nitrogen tetroxid, N_2O_4, is a brown gas with pungent odor, each molecule of which is entirely dissociated into two molecules of NO_2 at 150°. It may be condensed into a yellow liquid, boiling at 26°. It is soluble in water, reacting with it to form a mixture of nitrous and nitric acids according to the equation:

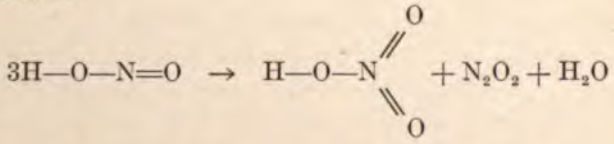
$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

It is a strong oxidizing agent, readily giving up half of its oxygen and breaking down into N_2O_2. Since the dioxid unites with the oxygen of the atmosphere to reform the tetroxid again, these substances act as "carriers" of oxygen and by their agency many compounds may be indirectly oxidized by the air which would not be oxidized directly without them.

Nitrogen pentoxid, N_2O_5, is a colorless, crystalline solid, melting at 30° and decomposing at 50° into nascent oxygen and N_2O_4. It is, therefore, a fine oxidizing agent. It dissolves in water, readily uniting with it to form HNO_3. It is, therefore, nitric acid anhydrid and to its presence the oxidizing action of nitric acid is due.

Nitrous Acid, HNO_2.

Nitrous acid is a compound of trivalent nitrogen, very unstable in character. It has never been obtained free and exists to a slight concentration only in aqueous solution. Acting as a weak monobasic acid, it forms salts which are quite stable both in and out of solution. On acidifying a solution of a nitrite, the free acid decomposes for the most part into water and the anhydrid, N_2O_3, the latter breaking down further, as previously stated. That part of the nitrous acid which does not decompose at once gradually changes into nitric acid according to the equation:



$$3\mathrm{H{-}O{-}N{=}O} \rightarrow \mathrm{H{-}O{-}N}\begin{smallmatrix} /\!\!/ \mathrm{O} \\ \backslash\!\!\backslash \mathrm{O} \end{smallmatrix} + N_2O_2 + H_2O$$

When **heated** gently, nitrites are unchanged but, when ignited, they break down into the oxids of nitrogen and the metal.

All nitrites are readily soluble with the exception of the silver salt and, on boiling with Na_2CO_3, they are transposed.

Nitrous acid, being so unstable, yields readily to chemical agents of either an oxidizing or reducing nature. With $KMnO_4$ and reagents of a similar nature, it is oxidized to nitric acid, each molecule of nitrous acid absorbing one atom of oxygen. On the other hand, strong reducing agents are oxidized by it, two molecules of nitrous acid giving up one atom of oxygen and breaking down into N_2O_2 and water (see pages 43 and 47). Thus *nitrous acid acts either as an oxidizing or reducing agent.*

The formation of nitrogen dioxid when nitrous acid acts as an oxidizing agent gives rise to the dark brown compound already referred to whenever nitrous acid and ferrous salts are brought together. As the nitrous acid oxidizes part of the ferrous iron to the ferric condition, the nitrogen dioxid, formed during the reaction, unites with the unoxidized ferrous salt according to the equations:

$$2C_6H_4(NH_2)_2 + HNO_2 \rightarrow NH_2C_6H_4N_2C_6H_3(NH_2)_2 + 2H_2O$$
$$2FeSO_4 + NO \rightarrow (FeSO_4)_2.NO$$

This and the following reactions are used as tests for nitrous acid.

Nitrous acid reacts with many organic compounds to form highly colored substances, some of which are used as dyes. With phenylenediamin in acid solutions, the well-known "Bismark Brown" dye is obtained, even a trace of nitrous acid giving a distinctly yellow-colored solution.

$$2C_6H_4(NH_2)_2 + HNO_2 \rightarrow NH_2C_6H_4N_2C_6H_3(NH_2)_2 + 2H_2O$$

With sulfanilic acid and naphtylamin a complex reaction of a similar nature takes place, resulting in the formation of compounds of an intense red color. With this reagent slight traces of nitrous acid produce a pink coloration.

The **nitrite ion, $\overset{-}{\mathrm{NO}}_2$**, is alone of importance. Some complex ions are formed of which the cobalti-nitrite ion, $Co(\overset{-}{NO}_2)_6$ (see page 231) is the best known.

The **barium ion, $\overset{++}{\mathrm{Ba}}$,** gives no precipitate with the nitrite ion, $\overset{-}{NO}_2$.

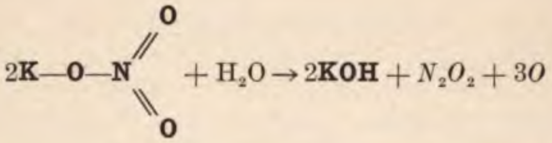
The **silver ion, $\overset{+}{\mathrm{Ag}}$,** gives a white crystalline precipitate only in concentrated solutions, for $AgNO_2$ is soluble in 300 parts of H_2O.

Nitric Acid, HNO_3.

Nitric acid is a compound containing pentavalent nitrogen corresponding to nitrous acid, which contains trivalent nitrogen. Like the latter, it is monobasic but, because of the higher state of the oxidation of the nitrogen it contains, its acid properties are much stronger. It is also much more stable and can be isolated from solution as a colorless, oily, fuming liquid boiling at 86°, with partial decomposition. It is miscible with water in all proportions, the boiling-point rising steadily as the proportion of water increases until at 120.5° a solution containing 68 per cent. of HNO_3 distills. This solution is ordinary "**concentrated nitric acid.**" If the solution is diluted beyond this point, the boiling point falls as the proportion of acid decreases until 100° is reached, the boiling-point of pure water, *i. e.*, of 0 per cent. HNO_3. Since all mixtures of nitric acid and water other than this 68 per cent. solution boil lower than 120.5°, if a solution of nitric acid is evaporated, it will tend to assume this definite composition, either by boiling off water, if it is less concentrated than 68 per cent., or HNO_3 if it is more concentrated.

"Concentrated nitric acid," on standing in the light, decomposes slowly into water, oxygen and nitrogen tetroxid which colors the solution yellow or brown. In dilute solution it is stable, however.

The **salts of nitric acid** are naturally less readily decomposed than the free acid. The most stable nitrates fuse without great decomposition. When strongly ignited, however, all decompose with the liberation of oxygen, becoming nitrites first, which later decompose into oxygen and oxids of the metal and of nitrogen. For this reason nitrates are much used as oxidizing agents for high-temperature reactions.



$$2\mathbf{K{-}O{-}N}\begin{array}{l}{}^{/\!\!/\,\mathbf{O}}\\ {}_{\backslash\!\backslash\,\mathbf{O}}\end{array} + H_2O \rightarrow 2\mathbf{KOH} + N_2O_2 + 3O$$

Heated on charcoal, all nitrates deflagrate, *i. e.*, the carbon is oxidized rapidly by the decomposing nitrate producing flashes of light and slight explosions.

All normal nitrates *are soluble.* Certain salts of nitric acid, such as bismuth and, to a less extent, mercury, react with water, *i. e.*, hydrolyze and form basic compounds which are quite insoluble. All nitrates are transposed by boiling with sodium carbonate.

Pure **nitric acid** *is one of the best oxidizing agents* known. The "concentrated" acid, also, possesses strong powers of oxidation. "Fuming" nitric acid is made by dissolving N_2O_4 in the ordinary concentrated acid. It possesses the additional oxidizing power of the tetroxid dissolved in it.

On diluting the acid with water, its oxidizing action decreases as its ionization increases. Concentrated nitric acid, for instance, oxidizes hydriodic acid very readily while dilute acid separates iodin only on long standing. In other words, as the concentration of undissociated acid falls, the oxidizing action decreases, indicating that the nitrate ion, $\overset{-}{NO}_3$, is much more stable than the undissociated acid, to which we must ascribe the greater part of its oxidizing properties.

To what degree nitric acid will part with its oxygen depends very greatly on temperature, concentration and the nature of the reducing substance. By abstracting various amounts of oxygen all the oxids of nitrogen can be theoretically formed, the element obtained and hydrogen finally added. All of these products can be formed practically. Strong reducing agents, such as nascent hydrogen, under suitable conditions carry the reduction all the way down to ammonia. Milder reducing agents will not carry it so far. Since the dioxid is the stablest of the nitrogen oxids, under ordinary conditions this is the usual reduction product and two molecules of nitric acid liberate three atoms of oxygen. (See pages 39 and 43.)

Since nitrogen dioxid is formed from both nitric acid and nitrous acid, the **test** with ferrous salts already outlined for nitrous acid (see page 149) may be used to detect nitric acid as well, the reactions being:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + N_2O_2 + 4H_2O$$
$$2FeSO_4 + NO \rightarrow (FeSO_4)_2.NO$$

Brucin dissolved in concentrated sulfuric acid is colored a deep-red by nitric acid (and chloric acid). The color changes rapidly to yellow and finally may become green.

The **nitrate ion, $\overset{-}{NO}_3$**, is the only known anion, for the reactions of which the alkali salts serve best.

The **barium ion, $\overset{++}{Ba}$,** produces no precipitate.

The **silver ion, $\overset{+}{Ag}$,** produces no precipitate.

PHOSPHORUS. P — 31.

The element exists in two well-known modifications.* Ordinary **phosphorus** is a very pale-yellow substance, almost transparent and of a hard waxy consistency at ordinary temperatures. It melts at 44.4° to a yellow liquid, which boils at 290°. In carbon disulfid it is very soluble but in other solvents it dissolves only sparingly, if at all. Yellow phosphorus is very reactive, uniting directly with all elements except nitrogen, carbon and the inert argon group. With the metals it forms phosphids which, on treatment with water or dilute acids, liberate PH_3. With oxygen it unites with especial readiness and it is necessary to keep it under water to protect it from the action of the atmosphere. Even under these conditions it becomes covered with an opaque white coating. In the air it glows with a pale light, plainly visible in a darkened room, very slight traces being sufficient to produce a marked "phosphorescence." At about 50° phosphorus is spontaneously inflammable, burning to the oxid, P_2O_5. Heated out of contact with the air to a temperature near its boiling-point, it is converted into the red modification.

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* Two other less common forms, a white and a black modification, are reported.

Red phosphorus is a dark granular powder which, being hygroscopic, tends to collect together in balls or become pasty. It does not melt but, when heated, sublimes, forming a vapor which condenses into liquid yellow phosphorus. It is not appreciably soluble in any solvent and at ordinary temperatures it is quite inert. By heat and other agents it may be forced to react and is then converted into the same compounds as the other modification.

Either form of phosphorus may be detected by burning and collecting the product of combustion in water, which may then be tested for phosphoric acid. Nitric acid will accomplish the same change but, with the yellow modification, concentrated acid acts explosively.

The **compounds of phosphorus** are those of an acid-forming element. The formation of halids and sulfids may be considered as indicating the possession of some metallic properties, but these bodies are entirely decomposed by water (hydrolyzed), forming, besides hydrohalogen or hydrosulfuric acids, hydroxids of phosphorus which are typical acids.

$$PCl_3 + 3H_2O \rightarrow 3HCl + P(OH)_3 \text{ (or } H_3PO_3)$$
$$PCl_5 + 5H_2O \rightarrow 5HCl + P(OH)_5 \text{ (or } H_3PO_4 + H_2O)$$

Phosphorus compounds, like those of nitrogen, are of two general types, trivalent and pentavalent, the former tending to oxidize readily into the latter. For this reason compounds of trivalent phosphorus are not of importance in analytical chemistry.

With **hydrogen,** several compounds are formed of which phosphin, PH_3, is the most important. Its reactions are very similar to those of NH_3 except that it is far more readily oxidized and is less basic. This point is indicated by the fact that PH_3 forms salts only with the strong halogen acids and these salts are decomposed by water with the liberation of phosphin. Phosphonium hydroxid, corresponding to NH_4OH, is unknown.

With **oxygen**, phosphorus forms P_2O_3 and P_2O_5 beside the less important P_4O and P_2O_4.

Phosphorus trioxid, P_2O_3, stands in the same relation to the pentoxid as does N_2O_3. Like the latter, it is an acid anhydrid, phosphorus acid, H_3PO_3 or, minus water, HPO_2, oxidizing readily to the higher form. Phosphorus trioxid exists to a large extent as the double molecule of the form $(P_2O_3)_2$. (See also arsenic and antimony, pages 156 and 165.)

Phosphorus pentoxid, P_2O_5, is a light snow-white powder, uniting with water with extreme readiness, forming phosphoric acid. Because of this property, phosphoric anhydrid is the best drying agent known to science.

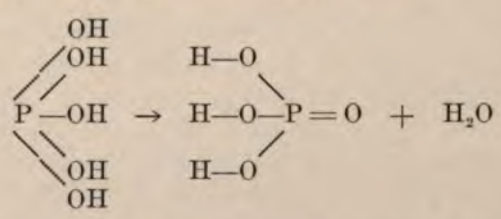
The simple **anion,** $\overset{\equiv}{P}$, is little known. United with oxygen, several ions are formed of which those given by phosphoric acid are the most important.

Phosphoric Acid.

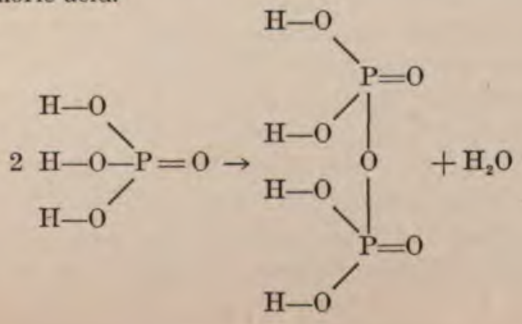
Phosphorus pentoxid reacts with water and, on long standing, may form phosphorus pentahydroxid in solution according to the equation:

$$\mathbf{P_2O_5} + 5H_2O \rightarrow 2P(OH)_5$$

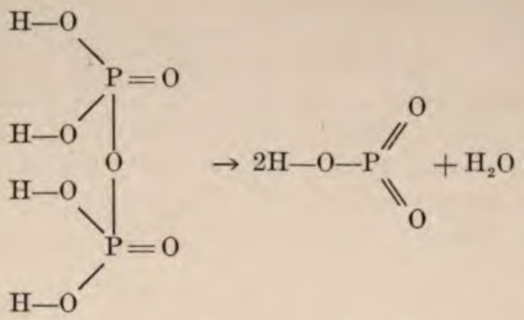
Such a compound cannot be separated from solution, however. Attempts to isolate it result in a compound containing one molecule less water, which is known as ortho-phosphoric acid.



On gentle heating, 255°, ortho-phosphoric acid loses water, forming pyro-phosphoric acid.



Pyro-phosphoric acid on further heating breaks down into meta-phosphoric acid.



These modifications of phosphoric acid are more stable than the similar modifications of arsenic (see page 163) or other acids and have an independent existence for a time in, as well as out of, solution.

Meta-phosphoric acid, HPO_3, is a colorless glassy-looking substance, which is often cast into sticks and known as "glacial" phosphoric acid. It is readily soluble, in aqueous solution acting as a monobasic acid, of which only the salts of the alkaline metals are readily soluble. It may be distinguished from the ortho and pyro acid by the facts that it gives white precipitates with $BaCl_2$ and $AgNO_3$ solutions and will coagulate egg albumen.

Pyro-phosphoric acid, $H_4P_2O_7$, resembles the meta acid in appearance but is much less common. It may be distinguished from the other forms of phosphoric acid by the fact that with $AgNO_3$ it gives a white precipitate, $Ag_4P_2O_7$, only in solutions which are nearly neutral. It does not coagulate white of egg and gives no precipitate with $BaCl_2$, except in an alkaline solution, when white $Ba_2P_2O_7$ falls.

Both of these partially-dehydrated acids, on long standing in aqueous solution, take up water slowly and form the ortho acid. The reaction is hastened by boiling and by the presence of a little dilute HNO_3, under which conditions they may be readily changed into the ortho form. For this reason they will not be considered further.

Ortho-phosphoric acid, H_3PO_4, is a colorless, crystalline solid, which is very hygroscopic and extremely soluble in water. It melts at 38.6°. It acts as a tribasic acid, forming salts of three types, primary, secondary and tertiary, which resemble the corresponding salts of arsenic acid (see page 163). All the alkaline phosphates (see page 66) are soluble. The primary salts of the alkaline earths and of magnesium are also soluble.

Other *phosphates are generally insoluble in water, but readily soluble in the stronger acids.* In acetic acid, which is of approximately the same strength as phosphoric acid, some phosphates are soluble, others insoluble.

Phosphoric acid (and an alkaline phosphate similarly) in solution dissociates in three steps as indicated:

$$H_3PO_4 \rightarrow \overset{+}{H} + H_2\overset{-}{P}O_4 \qquad (1)$$
$$H_2\overset{-}{P}O_4 \rightarrow \overset{+}{H} + H\overset{=}{P}O_4 \qquad (2)$$
$$H\overset{=}{P}O_4 \rightarrow \overset{+}{H} + \overset{\equiv}{P}O_4 \qquad (3)$$

The separation of $\overset{+}{H}$ ions according to the first step takes place sufficiently to make phosphoric acid an acid of fair strength. Ionization according to the second and third steps is so slight, however, that, were its strength dependent upon this dissociation primarily, phosphoric acid would have to be classed among the very weak acids.

In a solution of any phosphate, there will be a smaller concentration of the simple ion, $\overset{\equiv}{P}O_4$, than of the other ions formed according to the first or second steps. Nevertheless, when metallic ions are introduced into a solution containing all three of these phosphate ions, if a precipitate falls, it is generally of the type of normal salt formed by the simple $\overset{\equiv}{P}O_4$ ion even though it is present in much smaller concentration. For acid salts, such as would be formed by the ions, $H_2\overset{-}{P}O_4$ and $H\overset{=}{P}O_4$, are generally much more soluble, hence not so readily precipitated. The secondary salts of a few metals are quite insoluble and are precipitated on the addition of the phosphate ion. Magnesium, calcium, strontium and barium (see pages 93, 97, 97, 100) are of this class and precipitate normal phosphates of the type $Ba_3(PO_4)_2$ only from alkaline solutions.

The **barium ion, $\overset{++}{\mathbf{Ba}}$,** precipitates white $BaHPO_4$ from neutral solutions, soluble in acids, even in acetic acid. From alkaline solutions only, $Ba_3(PO_4)_2$ is precipitated. This salt is also soluble in acetic acid.

The **silver ion, $\overset{+}{\mathbf{Ag}}$,** precipitates yellow Ag_3PO_4, soluble in acids and in ammonium hydroxid.

These two reactions, together with the fact that egg albumen is not coagulated, serve to differentiate ortho-phosphoric acid from the pyro and meta acids.

The **magnesium ion, $\overset{++}{\mathbf{Mg}}$,** precipitates, from solutions containing ammonium as well as phosphate ions, white floccy $(NH_4)MgPO_4$ which, on boiling, becomes crystalline. It is readily soluble even in acetic acid. (See page 93.)

The **ferric ion, $\overset{+++}{\mathbf{Fe}}$,** precipitates straw-colored $FePO_4$ which, though readily soluble in the strong mineral acids, is insoluble in acetic and other organic acids. The $\overset{+++}{\text{Al}}$ and $\overset{+++}{\text{Cr}}$ ions give precipitates with similar properties. Phosphoric acid is often removed from solution by precipitating with ferric salts. (See pages 264 and 265.)

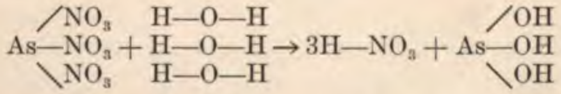
The **molybdate ion, $\overset{=}{\text{Mo}}\text{O}_4$,** does not unite directly with the phosphate ion. However, when a solution of ammonium molybdate, $(NH_4)_2MoO_4$, acidified with HNO_3, is added to a solution containing phosphoric acid, the latter combines with the anhydrid of molybdic acid, MoO_3, to form several complex phospho-molybdic acids, with compositions ranging from $H_3PO_4.10MoO_3$ to $H_3PO_4.14MoO_3$. Although these acids are soluble, their ammonium salts are insoluble in HNO_3, a reagent added to prevent the precipitation of any phosphate which might be insoluble in water or weaker acids. Under appropriate conditions, a yellow precipitate of the proportions $(NH_4)_3PO_4.12MoO_3$ can be obtained, the formula of which may be taken as representing the composition of the precipitate usually brought down. These complex phospho-molybdates are broken down in alkaline solutions into simple phosphates and molybdates of the alkali metals, all of which are readily soluble.

Similar complex bodies are formed by arsenic acid with MoO_3. (See page 164.)

ARSENIC. As — 75.

Arsenic, as it ordinarily occurs, is a crystalline gray substance with a metallic lustre. Under atmospheric pressure, it does not melt but sublimes, the vapor having a very characteristic garlic odor. At ordinary temperatures, it is but little acted on by the atmosphere but at 180° it burns readily with a bluish-white flame, forming the white trioxid, As_2O_3, the "white arsenic" of commerce. At ordinary temperatures, the molecule seems to double up and exists in the form $(As_2O_3)_2$.

The **element** is but little attacked by acids other than HNO_3. In dilute solutions of this acid, arsenic is soluble. Although no salts of acids containing oxygen are definitely known,* $As(NO_3)_3$ probably exists in solution to some extent. Because of hydrolysis, however, by far the greater part of the arsenic is present in the form of the hydroxid.



$$\text{As}\begin{matrix}\diagup\text{NO}_3\\ \text{—NO}_3\\ \diagdown\text{NO}_3\end{matrix} + \begin{matrix}\text{H—O—H}\\ \text{H—O—H}\\ \text{H—O—H}\end{matrix} \rightarrow 3\text{H—NO}_3 + \text{As}\begin{matrix}\diagup\text{OH}\\ \text{—OH}\\ \diagdown\text{OH}\end{matrix}$$

Concentrated HNO_3 acts as an oxidizing agent and oxidizes the trivalent arsenious compounds to pentavalent condition which are known as arsenic compounds. Possibly $As(NO_3)_5$ is first formed but, as the metallic properties of any element decrease as the valence rises (see page 45), this salt is hydrolyzed to an extent even greater than $As(NO_3)_3$, and practically all the arsenic exists in solution in the form of the pentavalent hydroxid. This compound loses one molecule of water, as shown in the equation, and exists in the partially dehydrated form:

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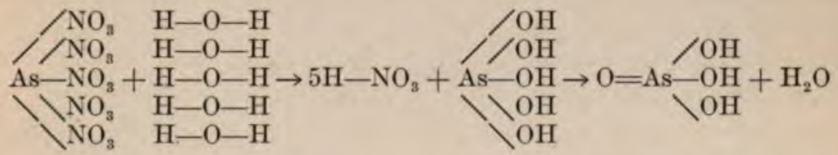
* Except the sulfate.



$$\begin{array}{l}\;\diagup NO_3\\ \diagup\diagup NO_3\\ As{-}NO_3\\ \diagdown\diagdown NO_3\\ \;\diagdown NO_3\end{array} + \begin{array}{l}H{-}O{-}H\\ H{-}O{-}H\\ H{-}O{-}H\\ H{-}O{-}H\\ H{-}O{-}H\end{array} \rightarrow 5H{-}NO_3 + \begin{array}{l}\;\diagup OH\\ \diagup\diagup OH\\ As{-}OH\\ \diagdown\diagdown OH\\ \;\diagdown OH\end{array} \rightarrow \begin{array}{l}\qquad\;\diagup OH\\ O{=}As{-}OH\\ \qquad\;\diagdown OH\end{array} + H_2O$$

While **trivalent arsenic** shows the properties of a weak base-forming element, **pentavalent arsenic** exhibits almost no basic qualities whatsoever, but does possess acid-forming properties quite strongly developed.

Of the **arsenic ions,** the trivalent kathion, $\overset{+++}{As}$, exists only to a small extent in solutions because of the great degree to which hydrolysis takes place. The pentavalent kathion, $\overset{+++++}{As}$, is practically unknown. Arsenic enters into the composition of several anions, of which those derived from arsenous and arsenic acids are the best known. These will be considered separately under appropriate headings.

Compounds of arsenic, of whatever nature, are readily reduced. Pentavalent compounds are rendered trivalent by mild reducing agents, such as H_2S and SO_2. More active **reducing agents** liberate the element itself, while the strongest reagents carry the reduction a step further and add hydrogen to it. (See page 39.)

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all compounds of arsenic are reduced to the metal, indicated by the presence of the characteristic garlic odor. The hot vapors oxidize as they leave the heated charcoal, however, and usually form a white coating of the oxid on cool objects.

Heated in a closed-tube with a mixture of 4 parts Na_2CO_3 to 1 part of **KCN,** all arsenic compounds are reduced to the element and a ring of black arsenic will sublime out of the mixture and condense on the cooler portions of the tube.

In the "wet way," **$SnCl_2$** causes a reduction to the element and precipitates arsenic as a dark-brown powder. Under the name of the **Bettendorf Test,** this reaction serves as a method of detecting arsenic. The reaction takes place only in the presence of strong HCl, however, hence an equal volume of concentrated HCl is added to the solution to be tested before adding the $SnCl_2$ which, for this purpose, is dissolved in concentrated HCl also. In dilute HCl solutions, the reduction will not take place.

Nascent hydrogen will reduce arsenic compounds to the lowest stage, *i. e.*, it will form arsenic hydrid, AsH_3, or arsin. This is a colorless, ill-smelling, exceedingly poisonous gas, analogous to NH_3 in composition but far less stable. Heated alone, it decomposes into arsenic and hydrogen. In the air, ordinarily, it burns to H_2O and As_2O_3. If, however, the amount of air is limited, it burns to H_2O and As.

The **Marsh Test,** the most delicate method known for detecting compounds of arsenic, depends on these reactions. It may be performed very satisfactorily as follows: Fit a six-inch test-tube with a stopper pierced with a short glass delivery-tube drawn out into a jet. In the bottom of the test-tube place a few pieces of zinc* and cover with about 10 ccm. of 4N H_2SO_4 made by mixing 1 volume of concentrated H_2SO_4 with 8 volumes of water. Place a little cotton in the mouth of the test-tube to hold back any moisture, insert the stopper loosely and, after allowing a moment's time for the hydrogen to replace all air in the test-tube, cautiously bring the jet to a flame and ignite the issuing gas. If a slight explosion occurs, it indicates that all of the air had not been driven out of the test-tube previously to igniting. Replace the cotton and stopper and wait a longer time for the hydrogen to replace the air completely, then bring to the flame as before. If the gas burns quietly, extinguish the flame, remove the stopper and cotton plug and introduce a few drops of the solution to be tested. Quickly replace the cotton and stopper and, after a moment, ignite the gas as it issues from the jet.†

If compounds of arsenic be present, arsin will be formed and will mix with the hydrogen and burn at the jet, giving the flame a bluish-white color and producing faint white clouds of As_2O_3. If a cold porcelain dish be held against the flame, thus limiting the supply of air, part of the arsenic will be deposited in the form of a velvety black stain which is very volatile and is readily soluble in NaOCl (difference from Sb; see page 166), sodium arsenate being formed.

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* Since As is very widely distributed in small amounts, many laboratory reagents, ordinary zinc especially, contain traces of it. In delicate work it is therefore necessary to make a "blank test" to ascertain whether the reagents to be employed are free from As. The method of procedure is exactly as described except that the solution to be tested is not added to the hydrogen generator. If no stain or mirror appears, the reagents contain no As, and anything which may develop later will be entirely due to the solution which is being tested.

† Or the delivery-tube may be made longer and the arsin decomposed by heating the tube in the middle portion. Under these conditions, the As is deposited as a brilliant mirror on the sides of the tube at some distance beyond the flame.

Metallic **copper** precipitates arsenic from solutions of its compounds strongly acidified with HCl, especially on warming. The arsenic unites with the copper, forming copper arsenid, Cu_5As_2, which is gray in color. This is known as the **Reinsch Test.** Since, however, silver, mercury, bismuth, gold, platinum, some sulfur compounds and certain organic substances may produce similar stains or deposits on copper, such an indication of arsenic must be confirmed by other tests.

The Arsenious Kathion, $\overset{+++}{As}$.

The **hydroxyl ion, $\overset{-}{OH}$**, added to a solution containing the $\overset{+++}{As}$ ion, produces no precipitate, as $As(OH)_3$ is fairly soluble. It is known only in solution, however, since all attempts to isolate it have resulted only in the dehydrated product, $(As_2O_3)_2$. This is soluble in water to a *slight* extent, forming the hydroxid again, but it dissolves in acids or alkalies more readily, since the salts formed by arsenic with either acids or bases are more soluble than the hydroxid. Arsenious hydroxid, AsO_3H_3, may ionize in two ways, either as a base into the ions $\overset{+++}{As}$ and $\overset{-}{OH}$, or as an acid into the ions $\overset{\equiv}{As}O_3$ and $\overset{+}{H}$. Its acidic nature is somewhat more strongly developed than the basic and its solutions in pure water have a slight acid reaction. In alkaline solutions the high concentration of $\overset{-}{OH}$ ions causes a repression of its dissociation as a base, while in acid solutions the high concentration of $\overset{+}{H}$ ions causes a repression of its ionization as an acid. (See page 31.)

Consequently, in acid solutions, it acts as a base while in alkaline solutions it behaves as an acid. In acid solutions, the $\overset{+}{H}$ ions unite with the $\overset{-}{OH}$ ions separated by AsO_3H_3 to form undissociated water and cause a continual reduction of the concentration of the $\overset{-}{OH}$ ions necessary to maintain equilibrium. Hence AsO_3H_3 continually dissociates into $\overset{+++}{As}$ and $\overset{-}{OH}$ ions and thus is forced to show a basic character (see page 36). The properties and reactions of AsO_3H_3, acting as an acid, will be considered later.

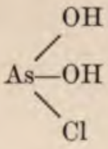
The **carbonate ion, $\overset{=}{CO}_3$**, has no effect on the $\overset{+++}{As}$ ion, since arsenic carbonate is unknown. Alkaline carbonate solutions are always hydrolyzed and contain the $\overset{-}{OH}$ ion. For this reason, carbonate solutions have the same action as alkaline hydroxids, but in a smaller degree.

The **sulfid ion, $\overset{=}{S}$**, gives a precipitate of yellow As_2S_3 from acid solutions only; from alkaline solutions no precipitate is thrown down because of the formation of soluble salts of thioacids (see page 162). Solutions of As_2O_3, to which neither acid nor alkali have been added, color slightly when H_2S is introduced, owing to the formation of a colloidal precipitate. They remain perfectly clear and transparent, however, and will pass through the finest filter paper. On boiling, or on the addition of a strong electrolyte, As_2S_3 is precipitated in the usual form. (See page 37.)

The $\overset{+}{H}$ ion has no effect on As_2S_3, but HNO_3 oxidizes it to H_3AsO_4. In alkalies and their sulfids and in ammonium carbonate, As_2S_3 is soluble, forming salts of thioacids. (See page 162.)

The **sulfate ion, $\overset{=}{SO}_4$**, produces no precipitate, as the sulfate is soluble, especially in the slightly acid solutions necessary to prevent the formation of insoluble basic salts. Other salts of oxygen acids are unknown.

The **chlorid ion, $\overset{-}{Cl}$**, and other halid ions produce no precipitate, since the halid salts of arsenic are soluble. Arsenious chlorid, $AsCl_3$ is an oily liquid, B. P. 130°. Dissolved in a little water, it hydrolyzes into the basic salt,



In dilute solutions, it separates into the hydroxid and HCl almost entirely, owing to the mass action of the water. If HCl be added to a dilute solution, however, because of the increased concentration, $AsCl_3$ is formed again in proportion to the excess of acid added. An equilibrium exists which may be represented by the equation:

$$2AsCl_3 + 3H_2O \leftrightarrow 2As(OH)_3 + 6HCl$$

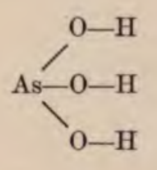
Because of these and similar reactions, if any arsenious compound be heated with HCl, it will be changed into $AsCl_3$ which, being volatile, will be gradually driven off.

Arsenic Compounds.

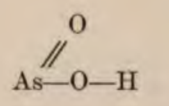
Pentavalent arsenic compounds are all of an acid nature. No salts of oxygen acids are known. The halids are entirely decomposed by water. The sulfid, As_2S_5, is not decomposed by water, but may be precipitated from acidified solutions of pentavalent arsenic compounds by H_2S. It is yellow in color, less stable than the trisulfid, into which is slowly decomposes with the separation of sulfur. It is insoluble in acids generally, but is oxidized by HNO_3 and other oxidizing agents to H_3AsO_4 and H_2SO_4 (or free sulfur, see page 50). It dissolves in alkalies, alkaline sulfids and ammonium carbonate, forming salts of thioacids analogous to those of trivalent arsenic. (See page 164.)

Arsenius Acid.

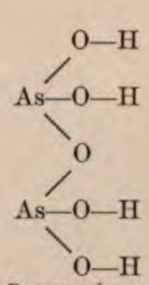
Arsenious hydroxid, $As(OH)_3$, shows more acidic properties than basic properties, and is ordinarily known as arsenious acid and written H_3AsO_3. As already stated, it exists only in solution and, on any attempt to isolate it, separates water and gives the oxid which thus becomes arsenious acid anhydrid. But slightly soluble in water, $(As_2O_3)_2$ dissolves readily in alkaline solutions, forming salts of which three types are known. They are derived from the hypothetical arsenious acids represented by the formulae:



Ortho-arsenious acid.



Meta-arsenious acid.



Pyro-arsenious acid.

These acids differ only in the extent to which they are hydrated. All are very weak and, even in dilute solution, but few arsenious anions are found.

Ortho-arsenites are not very stable, Ag_3AsO_3 being the only well-known example. Salts formed from solutions are generally of the meta-type, $MAsO_2$, although some pyro-arsenites are definitely known.

All arsenites, with the exception of salts of the alkalies, are soluble with difficulty in water, but, like salts of weak acids, generally are readily soluble in the strong mineral acids.

All arsenites are transposed by boiling with Na_2CO_3 according to the equation for a typical reaction:

$$2\mathbf{Ag_3AsO_3} + 3Na_2CO_3 \rightarrow \mathbf{3Ag_2CO_3} + 2Na_3AsO_3$$

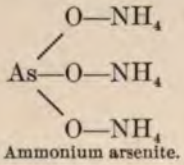
The **barium ion, $\overset{++}{Ba}$,** added to a solution containing an arsenite, precipitates white barium meta-arsenite, $Ba(AsO_2)_2$, readily soluble in dilute acids.

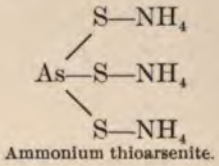
The **silver ion, $\overset{+}{Ag}$,** precipitates yellow (difference from H_3AsO_4, see page 164) silver ortho-arsenite, like all salts of arsenious acid soluble in dilute acids, like most silver salts soluble in NH_4OH (see page 85). Hence it requires a distinctly neutral solution for its precipitation.

The **magnesium ion, $\overset{++}{\mathbf{Mg}}$,** in the presence of ammonium salts, gives no precipitate (difference from H_3AsO_4).

The **molybdate ion, $\mathbf{M\bar{o}O_4}$**, produces no precipitate (difference from H_3AsO_4).

The **salts of thioarsenious acid** are very analogous to the salts of arsenious acid and may be considered as derived from the latter by the substitution of sulfur for oxygen, as shown by the formulae:


Ammonium arsenite.


Ammonium thioarsenite.

Salts of this nature are formed when arsenious sulfid is dissolved in alkalies, alkaline sulfids or in ammonium carbonate, and, also, when H_2S is passed into an alkaline solution of arsenious acid, as is shown by the following reactions:

$$\mathbf{As_2S_3} + 6KOH \rightarrow K_3AsS_3 + K_3AsO_3 + 3H_2O$$
$$\mathbf{As_2S_3} + 3(NH_4)_2S^* \rightarrow 2(NH_4)_3AsS_3$$
$$\mathbf{As_2S_3} + 3(NH_4)_2CO_3 \rightarrow (NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 3\mathit{CO_2}$$
$$2Na_3AsO_3 + 3H_2S \rightarrow Na_3AsS_3 + Na_3AsO_3 + 3H_2O$$

On acidifying a solution of a thioarsenite, thioarsenious acid, H_3AsS_3, is first formed but, just as arsenious acid splits out H_2O and forms As_2O_3, so thioarsenious acid splits out H_2S and forms As_2S_3:

$$2H_3AsO_3 \rightarrow \mathbf{As_2O_3} + \mathit{3H_2O}$$
$$2H_3AsS_3 \rightarrow \mathbf{As_2S_3} + \mathit{3H_2S}$$

Consequently, on acidifying a solution of a thioarsenite, As_2S_3 is precipitated. Because of the possible formation of soluble salts of thioarsenious acid, it is necessary to acidify strongly with HCl a solution of an arsenite, if it is desired that As_2S_3 be precipitated by introducing H_2S.

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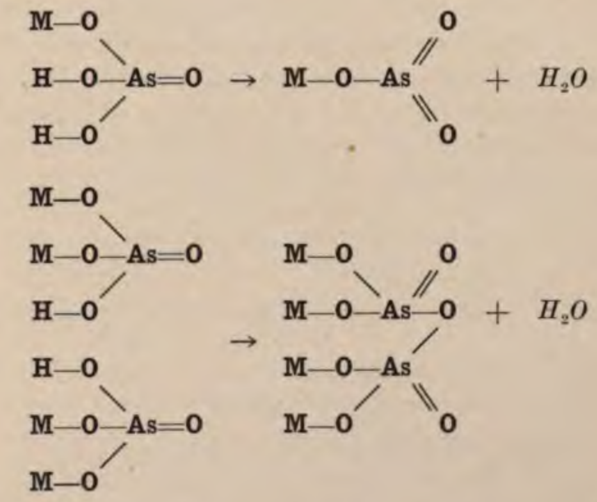
* If a yellow polysulfid be used instead of a colorless monosulfid, the excess of sulfur will oxidize the thioarsenite over to the corresponding thioarsenate.

$$As_2S_3 + 3(NH_4)_2S.xS \rightarrow 2(NH_4)_3AsS_4 + (3x-2)S$$

Arsenic Acid.

Pentavalent arsenic compounds, as previously stated, have a well-developed acidic character, the pentavalent hydroxid being ordinarily known as arsenic acid. It is most readily formed by the oxidation of arsenious oxid in the presence of water. On evaporation, **ortho-arsenic acid, H_3AsO_4**, is obtained as a white, crystalline powder, readily losing water on heating, giving $H_4As_2O_7$, pyro-arsenic acid, and $HAsO_3$, meta-arsenic acid. On dissolving in water, the dehydrated acids take up water again.

The **salts of ortho-arsenic acid** are of three types,—primary, secondary and tertiary—depending on the amount of hydrogen replaced by metal. Primary salts on heating form meta-arsenates, and secondary salts pyro-arsenates.



Solution in water causes hydration, as in the case of the acids; hence, the acid and its salts are always of the ortho- form in solution.

Arsenic acid, although dissociating to a greater degree than arsenious acid, cannot be considered strong, and its alkali salts show hydrolytic phenomena to a greater extent than the corresponding salts of phosphoric acid, to which it is very similar.

Of the **salts of arsenic acid,** those formed by the alkali metals are readily soluble. Others are generally insoluble in water, but readily soluble in mineral acids.

All arsenates are transposed by boiling with sodium carbonate.

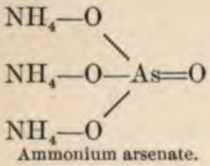
The **barium ion, $\overset{++}{\mathbf{Ba}}$,** added to a solution containing an arsenate, produces a white precipitate of $Ba_3(AsO_4)_2$, soluble in dilute acids.

The **silver ion, $\overset{+}{\mathbf{Ag}}$,** precipitates chocolate-colored (difference from H_3AsO_3, see page 161) Ag_3AsO_4, very soluble in dilute acids and in NH_4OH, requiring a distinctly neutral solution for its precipitation.

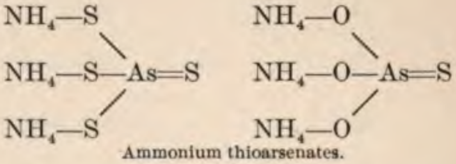
The **magnesium ion, $\overset{++}{\mathbf{Mg}}$,** from solutions containing the ammonium ion as well, precipitates white $(NH_4)MgAsO_4.6H_2O$, which may be rendered beautifully crystalline by boiling or by being brought down slowly from solution. The presence of NH_4Cl aids the transformation from the flocculent to the crystalline form.

The **molybdate ion, $\mathbf{M\overset{-}{o}O_4}$,** from solutions of the ammonium or other similar salt, causes a yellow precipitate to fall which has the composition represented by the formula, $(NH_4)_3AsO_4.12MoO_3.4H_2O$. This is to be regarded as the ammonium salt of a very complex arseno-molybdic acid. It is insoluble in HNO_3, but in alkaline solutions it dissolves readily.

The **salts of the thioarsenic acids** are very analogous to the ordinary arsenates and resemble closely the salts of thioarsenious acid. Two types are recognized, depending on the proportion in which the oxygen of arsenates has been substituted by sulfur. In one form, all of the oxygen has been replaced by sulfur; in the other, only one-quarter, as is shown by the formulae:



Ammonium arsenate.



Ammonium thioarsenates.

Salts of thioarsenic acid are formed by dissolving arsenic sulfid, As_2S_5, in alkalies, alkaline sulfids or ammonium carbonate; by dissolving arsenious sulfid, As_2S_3, in alkaline polysulfids; or by passing H_2S into a solution of an arsenate which has not been acidified. The following equations indicate the reactions taking place:

$$\mathbf{As_2S_5} + 6KOH \rightarrow K_3AsS_4 + K_3AsO_3S + 3H_2O$$
$$\mathbf{As_2S_5} + 3(NH_4)_2S \rightarrow 2(NH_4)_3AsS_4$$
$$\mathbf{As_2S_5} + 3(NH_4)_2CO_3 \rightarrow (NH_4)_3AsS_4 + (NH_4)_3AsO_3S + 3CO_2$$
$$\mathbf{As_2S_3} + 3(NH_4)_2S.xS \rightarrow 2(NH_4)_3AsS_4 + (3x-2)S$$
$$2Na_3AsO_4 + 5H_2S \rightarrow Na_3AsS_4 + Na_3AsO_3S + 5H_2O$$

On acidifying a solution of a thioarsenate, **thioarsenic acid, $\mathbf{H_3AsS_4}$** (or H_3AsO_3S), is first formed, but it immediately decomposes into As_2S_5

and H_2S, analogously to the manner in which arsenic acid may be broken down into As_2O_5 and H_2O.

$$2H_3AsO_4 \rightarrow \mathbf{As_2O_5} + 3H_2O$$
$$2H_3AsS_4 \rightarrow \mathbf{As_2S_5} + 3H_2S$$

On acidifying a solution of a thioarsenate, therefore, As_2S_5 is precipitated. These reactions make evident the reason why arsenic sulfid is best precipitated from solutions quite strongly acid with HCl. On passing H_2S into an acidified solution of an arsenate, the precipitate usually obtained consists of As_2S_5, As_2S_3 and free sulfur, indicating that the H_2S acts partly as a reducing agent as well as a precipitant.

ANTIMONY (Stibium). Sb—120.2.

Antimony is a white, crystalline, very brittle metal. It does not tarnish in the air, but, when heated, burns with a greenish-white flame to the white trioxid, Sb_2O_3, which, except at extremely high temperatures, has the double molecule, $(Sb_2O_3)_2$, like the corresponding oxid of arsenic. The trioxid readily absorbs more oxygen, if heated, and becomes Sb_2O_4.

The metal is not ordinarily acted upon by acids with any readiness even when heated. The oxidizing action of HNO_3 is more affective than HCl or H_2SO_4 and results in the formation of $(Sb_2O_3)_2$ in dilute, and Sb_2O_5 in concentrated solutions. Aqua regia is the only satisfactory solvent, however, converting the metal into chlorids.

Antimony requires the expenditure of a small amount of energy to make the metal pass into the ionic condition, hence it is precipitated from solutions of its salts by several other metals, especially zinc, which shows a greater tendency to become ionic. The element shows a valence of three and five, and, as is always the case, compounds showing the lower valence act more like metallic compounds than those of higher valence. Trivalent antimony shows considerably more basic properties than trivalent arsenic, but its acid properties are not so well developed. Pentavalent antimony acts as a very weak base-forming element, no salts of oxygen acids being known. Its acid properties are not so striking as those of pentavalent arsenic. Since the trivalent compounds pass quite readily into the higher form in the presence of oxidizing agents, they are to be regarded as reducing substances.

Under the influence of **reducing agents,** antimony compounds behave just as do the compounds of arsenic.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all antimony compounds are reduced to the metal, leaving a bright white globule which is exceedingly brittle (difference from Sn, Pb, and Ag), does not dissolve in HNO_3 (difference from Pb, Ag and Bi) but is changed to a white powder (like Sn). It will not dissolve appreciably in hot concentrated HCl (distinction from Sn) and passes into solution only on treatment with aqua regia. On diluting, H_2S gives an orange precipitate. Since the metal oxidizes readily, a coating of white oxid forms on the charcoal near to the melt. The fumes are odorless, thus differentiating them from arsenic.

Nascent hydrogen acting on any soluble antimony compound in acid solution forms stibin, SbH_3. In alkaline solutions, it does not form (distinction from As). It is very similar to AsH_3, and, like it, is decomposed on heating in a glass tube into hydrogen and the metal. Since stibin is less stable than arsin and antimony is less volatile than arsenic, the deposit will appear much nearer to and usually on both sides of the flame. Stibin burns with a greenish-white flame to the oxid but, in a limited supply of air, deposits on cold porcelain held in the flame metallic antimony which, unlike the brown velvety stain produced by arsenic, is black and metallic in appearance and will not dissolve in NaOCl.

All the **salts of antimony** hydrolyze very decidedly and tend to precipitate oxy-compounds from solutions. For this reason, no simple salts of antimony are soluble in water in the ordinary sense, but the halids are quite soluble in the presence of a small per cent. of acid.

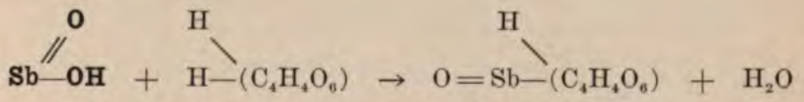
Of the **antimony ions,** $\overset{+++}{Sb}$ is best known. The pentavalent kathion is unknown. Antimony is a constituent of several anions, of which $\overset{-}{Sb}O_3$ and $\overset{-}{Sb}O_4$ may be considered typical. Corresponding to these are the thio ions $\overset{-}{Sb}S_3$ and $\overset{-}{Sb}S_4$. The antimonate ions, in which the element shows a valence of five, are better known than the antimonite ions. Complex anions are well known. Of these, the antimony-tartrate ion, $SbO(\overset{-}{C}_4H_4O_6)$ is the most important.

The reactions of the $\overset{+++}{Sb}$ ion may be most satisfactorily studied by using slightly acid solutions of the chlorid.

The Antimonous Ion, $\overset{+++}{Sb}$.

The **hydroxyl ion, $\overset{-}{O}H$,** added to a solution containing the $\overset{+++}{Sb}$ ion, precipitates $Sb(OH)_3$ which loses water in various proportions, forming finally $(Sb_2O_3)_2$. All of these dehydration products are capable of separating both $\overset{+}{H}$ and $\overset{-}{O}H$ ions, the former being called forth in alkaline solutions especially, the latter in the presence of acids. For this reason, the precipitate is somewhat soluble in alkalies as well as in acids. Solutions in pure water react slightly acid, hence the hydroxid is sometimes called ortho-antimonous acid. The partially-dehydrated substances correspond to the pyro- and meta- acids. The latter has never been definitely isolated, however. Of the salts of the various antimonous acids but little is definitely known. Certain ones of the meta type, M — O — Sb = O, exist but, as none are important, they will not be further considered.

Antimonous hydroxid or oxid is readily soluble in tartaric acid, forming a complex antimony-tartrate ion, $SbO(\bar{C}_4H_4O_6)$, many compounds of which are soluble.



$$\overset{O}{\overset{/\!/}{\mathrm{Sb}}}\mathrm{-OH} + \overset{\mathrm{H}\searrow}{\mathrm{H-(C_4H_4O_6)}} \rightarrow \overset{\mathrm{H}\searrow}{\mathrm{O{=}Sb-(C_4H_4O_6)}} + \mathrm{H_2O}$$

Bodies containing the univalent radicle, (O = Sb —), are known as antimonyl compounds. The potassium antimonyl-tartrate is the most important and is known as "tartar emetic" because of its medicinal action. At ordinary temperatures, this complex salt is soluble in about 8 parts of water. The antimonyl-tartrate ion is quite stable in the presence of $\bar{O}H$ ions. Hydrogen ions tend to decompose it and, in acid solutions, the reactions of the $\overset{+++}{Sb}$ ion predominate. On adding HCl, the oxychlorid is precipitated. Nitric or sulfuric acid bring down the hydroxid because of hydrolysis of the sulfate and nitrate first formed. From acid "tartar emetic" solutions, the same precipitate falls when the $\bar{\bar{S}}$ ions is introduced as from $SbCl_3$ solutions. Similar antimonyl ions are formed with citric and other organic acids.

The **carbonate ion, $\bar{\bar{CO}}_3$**, produces the same precipitate as the $\bar{O}H$ ion for, since antimony carbonate is unknown, it is the $\bar{O}H$ ions formed by hydrolysis which are the active agents in solution.

The **sulfid ion, $\bar{\bar{S}}$,** precipitates orange Sb_2S_3, soluble in alkalies and in alkaline sulfids and polysulfids, forming compounds similar to those of arsenic (see page 160). Unlike As_2S_3, the precipitate is soluble in hot HCl and insoluble in $(NH_4)_2CO_3$. On fusion, it turns black and crystallizes in the form of the natural sulfid, stibnite.

The **sulfate ion, $\bar{\bar{SO}}_4$**, produces no precipitate, since $Sb_2(SO_4)_3$ is soluble in dilute acid solutions.

The **chlorid ion, $\bar{Cl}$,** produces no precipitate, since $SbCl_3$ and other halids are soluble in dilute acid solutions. Antimony trichlorid forms usually a colorless crystalline mass, which, because of its softness at ordinary temperatures, is known as "butter of antimony." When treated with about twice its weight of water, it hydrolyzes and forms SbOCl, but, if diluted, the mass action of the water disturbs this equilibrium and hydrolysis takes place to a greater degree, resulting in an admixture of the oxid with the oxychlorid. This is a reversible reaction, however, and the precipitate dissolves as the concentration of HCl increases, and forms again on dilution. The precipitate is soluble in tartaric acid and alkaline tartrates, forming the complex antimonyl-tartrates. It is also somewhat soluble in alkalies, forming salts of antimonous acid.

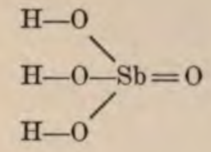
The **thioantimonites** correspond to the salts of antimonous acid, as do the thioarsenites to the arsenites. They are in every way analogous to the thioarsenites in properties, reactions and methods of formation. The ion $\overset{\equiv}{Sb}S_3$ is unstable in acid solution and, on acidifying a solution of a thioantimonite, H_2S and Sb_2S_3 is precipitated as in the case of thioarsenites. (See page 162.)

Pentavalent Antimonic Compounds.

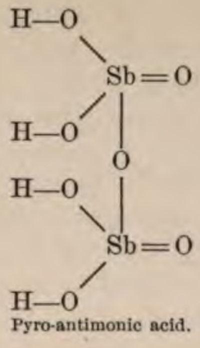
Pentavalent antimony acts much less as a base-forming element than when it is in the trivalent condition, hence no salts of oxygen acids are known and all salts hydrolyze to even a greater extent than with antimonous compounds. A higher percentage of acid is required to keep them in solution. Antimony pentachlorid, $SbCl_5$, is a yellow fuming liquid, soluble in moderately concentrated HCl, but, in such solution, exists practically as undissociated salt. On treatment with H_2S in the cold, orange Sb_2S_5 can be precipitated. Under ordinary conditions, the precipitate consists of Sb_2S_5, Sb_2S_3 and free sulfur, thus indicating that a partial reduction to the lower condition has been caused by the H_2S. Antimony pentasulfid is soluble in concentrated HCl, in alkalies and alkaline sulfids and polysulfids, forming thioantimonates. In the ordinary solution of $(NH_4)_2CO_3$, when heated, it is somewhat soluble. In the cold it is insoluble, however, and may be differentiated in this way from the sulfids of arsenic. (See page 160.)

Antimonic Acid.

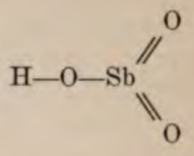
The pentavalent hydroxid of antimony, $Sb(OH)_5$, does not exist but various dehydration products are known. Since these all possess well-defined acid properties, they are ordinarily called antimonic acids. Three forms are recognized, corresponding exactly with the arsenic acids.



Ortho-antimonic acid.



Pyro-antimonic acid.



Meta-antimonic acid.

Many salts of these acids are known, generally of the pyro- and meta-types. Since the antimonic acids are all weak, the salts all hydrolyze considerably and are generally of but little importance. The acid sodium pyroantimonate, $Na_2H_2Sb_2O_7$, is of interest because of the fact that it is one of the most insoluble simple sodium salts known. It requires about 400 parts of water to dissolve it. The corresponding potassium salt is more soluble and precipitates the sodium salt when the $\overset{+}{Na}$ ion is introduced. This is sometimes used as a test for sodium salts.

The **barium ion, $\overset{++}{Ba}$,** added to a solution containing an antimonate, precipitates white $Ba(SbO_3)_2$.

The **silver ion, $\overset{+}{Ag}$,** precipitates $AgSbO_3$, readily soluble in acids and in NH_4OH.

Thioantimonates are better known than most other salts of thioacids. In general, they correspond closely with thioarsenates (page 164) in properties and methods of formation. The thioantimonate ion, $S\overline{b}S_4$, is no more stable in acid solutions than is the ion $A\overline{s}S_4$, and the acid decomposes into H_2S and Sb_2S_5, just as the thioacids of arsenic do. The most important compound of this type is known as "Schlippe's salt" and has the composition indicated by the formula $Na_3SbS_4.9H_2O$.

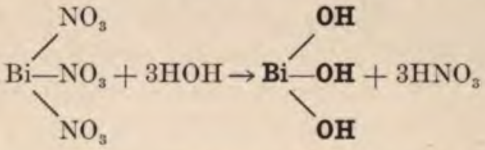
BISMUTH. Bi — 208.5.

Bismuth is a very brittle, crystalline metal of a reddish-white color. At ordinary temperatures it is not tarnished by any constituent of the atmosphere, but, at higher temperatures, it unites with oxygen, forming pale yellow bismuth trioxid, Bi_2O_3.

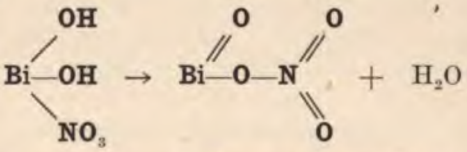
The metal is but little soluble in dilute HCl or H_2SO_4. Dilute HNO_3 has some action. In hot concentrated H_2SO_4 or fairly strong HNO_3 it dissolves readily. The element absorbs a small amount of energy in passing from the metallic into the ionic condition, therefore its salts may be reduced without difficulty. The metal is precipitated from solutions of its salts by metallic zinc.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all bismuth salts are reduced, leaving a bright metallic globule which is brittle (difference from Ag, Pb, and Sn). A coating—orange-yellow, hot; lemon-yellow, cold (difference from Pb and Sn)—is formed on the charcoal, due to oxidation of part of the metal. The globule is soluble in warm, fairly concentrated HNO_3 and, with HCl, gives a precipitate (if at all) only in very dilute solutions (difference from Ag and Pb). This precipitate is soluble in a slight excess of acid and may by this means be further differentiated from lead and silver.

Salts of bismuth are generally colorless. None of them dissolve readily in pure water, owing to the formation of insoluble oxysalts. Bismuth acts as a very weak, trivalent, base-forming element, hence its salts hydrolyze very considerably. The regular equation would be:



Hydrolysis is, however, a typical reversible reaction, for bismuth hydroxid is soluble in HNO_3 with the formation of the nitrate and water. Hence a condition of equilibrium ensues in which both bismuth hydroxid and nitrate are present. The mixture seems to be within the molecule (see page 21), however, and basic bismuth nitrate results. This loses water, as the equation shows, and forms the oxysalt which is known as the "subnitrate."



To prevent the precipitation of salts of this character, an acid must be present in the solution. In the presence of a little of their respective acids, the chlorid, sulfate and nitrate all dissolve readily. For this reason, all bismuth salt solutions react strongly acid to litmus.

The only **bismuth ion** is $\overset{+++}{\mathbf{Bi}}$. This shows little tendency toward the formation of complex ions, hence bismuth reactions are for the most part normal. The nitrate, chlorid or sulfate are satisfactory solutions for studying the reactions of the $\overset{+++}{\text{Bi}}$ ion.

The **hydroxyl ion, $\overset{-}{\mathbf{OH}}$,** gives a flocculent precipitate of white $Bi(OH)_3$, under ordinary conditions insoluble in an excess of alkaline hydroxids. In hot concentrated KOH or NaOH it is slightly soluble, however, thus showing a tendency to act as an acid-forming element.* On boiling, $Bi(OH)_3$ loses water and forms $Bi<\substack{O\\OH}$ which is slightly yellowish in color. On further heating, Bi_2O_3 is formed.

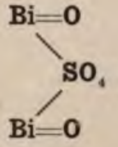
When heated with an alkaline solution of sodium stannite, Na_2SnO_2, the oxid or hydroxid turns black, owing to the formation of a mixture of a lower oxid, BiO, and of metallic bismuth, both of which are black. The tin is oxidized as the bismuth is reduced, according to a reaction which may be written so as to express both stages of the reduction:

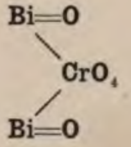
$$\mathbf{Bi_2O_3} + 2Na_2SnO_2 \rightarrow \mathbf{BiO} + \mathbf{Bi} + 2Na_2SnO_3$$

The **carbonate ion, $\overset{=}{\mathbf{CO}}_3$,** brings down basic bismuth carbonate, owing to hydrolysis of the precipitating reagent.

The **sulfid ion, $\overset{=}{\mathbf{S}}$,** precipitates brownish-black Bi_2S_3, soluble in HNO_3 due to oxidation to $Bi(NO_3)_3$ and free sulfur, but otherwise insoluble in acids. Unlike antimony, arsenic and tin, the acid properties of bismuth are not sufficiently developed to allow the formation of salts of this acid, therefore, Bi_2S_3 is not soluble in alkalies or alkaline sulfids.

The **sulfate ion, $\overset{=}{\mathbf{SO}}_4$,** causes no precipitate, since $Bi_2(SO_4)_3$ is soluble. An oxysalt, with the formula given below, forms readily in dilute solutions.





The **chromate ion, $\overset{=}{\mathbf{CrO}}_4$,** precipitates a yellow oxychromate (formula given above), soluble in HNO_3 but insoluble in NaOH and thereby differentiated from yellow $PbCrO_4$ which is soluble.

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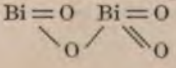
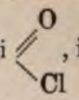
* A few compounds are known in which bismuth is pentavalent. According to the general rule, as the valence rises the acidic properties develop. The compound $H-O-Bi\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$, similar to $H-O-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ and $H-O-P\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$, is known as bismuthic acid. It is of a bright red color and forms salts, among which an oxid Bi_2O_4 (or BiO_2) is to be considered as the oxy bismuth salt of bismuthic acid, as its structural formula indicates,



The **chlorid ion, $\bar{\mathrm{C}}\mathrm{l}$,** gives no precipitate, since $BiCl_3$ is soluble. The tendency toward the formation of bismuth oxychlorid,  $\mathrm{Bi}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \diagdown\mathrm{Cl}\end{array}$, is very marked whenever the concentration of acid becomes sufficiently low to permit hydrolysis to take place. A beautiful illustration of the phenomena of equilibrium and mass action may be obtained by diluting cautiously a $BiCl_3$ solution until a precipitate forms. This will dissolve on the addition of a drop or two of concentrated HCl, to be precipitated again as soon and as often as the concentration of acid falls below the equilibrium requirement because of dilution. Since bismuth is more of a base-forming element than antimony, the precipitated BiOCl is far more soluble in acid than the similar salt, SbOCl, which it closely resembles. Since bismuth is less of an acid-former than antimony, BiOCl is insoluble in alkalies, while SbOCl dissolves readily. Bismuth oxychlorid is insoluble in tartaric acid, $H_2(C_4H_4O_6)$, and is turned black by H_2S, whereas SbOCl is soluble in tartaric acid and is turned orange by H_2S.

The **iodid ion, $\bar{\mathrm{I}}$,** precipitates black BiI_3 from fairly concentrated solutions. From dilute solutions, orange BiOI falls, an oxyiodid similar to BiOCl. Bismuth tri-iodid is soluble in excess of alkaline iodids forming the complex ion, $\mathrm{B\bar{i}I_4}$, which decomposes on dilution into the simple ions with the precipitation of black BiI_3 first and later of orange BiOI.

The **cyanid ion, $\overline{\mathrm{CN}}$,** probably forms $Bi(CN)_3$ at first, but this is hydrolyzed completely and $Bi(OH)_3$ is precipitated. No simple cyanids of trivalent metals are known.

The **phosphate ion, $\mathrm{P}\bar{\bar{\bar{\mathrm{O}}}}_4$,** precipitates white granular $BiPO_4$ which is interesting from the fact that, unlike all ordinary phosphates, it is not readily soluble in solutions of the strong acids.

Group 5, Second Type.

Vanadium 51.2; Niobium 94; Tantalum 183.

Three rare elements are the only known members of this type. In general, they resemble those elements of the first type which have medium atomic weights and they will not be considered further.

Group 6, First Type.

Oxygen 16; **Sulfur 32.1;** Selenium 79.2; Tellurium 127.6.

The elements of Group 6 show characteristic valences of six or two. The members of this and the following group, however, are capable of forming compounds in which the elements exhibit valences intermediate between those which are considered as most characteristic. Inasmuch as the properties of the compounds change as the valence of the element rises, compounds of widely different nature may be formed by the same element.

The members of this group are light non-metallic elements, not particularly active at ordinary temperatures but, as the temperature rises, they unite readily with most other elements. For these reasons, they are found in nature both free and combined. Hydrids, of the type H_2O, are well known and important. They possess the properties of very weak acids. Combination with oxygen takes place readily in various proportions, oxids being formed which act as acid anhydrids. These unite with water, forming acids, the strength of which increases as the valence of the element in them rises, those of the sulfuric acid type, H_2SO_4, being much stronger than the sulfurous acid type, H_2SO_3.

Selenium and tellurium are not of common occurrence and they will not be considered further.

OXYGEN. O — 16.

Oxygen is a colorless, odorless gas, occurring free in the atmosphere to the extent of about 21 per cent. by volume. In combination with other elements, it is estimated that oxygen constitutes about 50 per cent. of the known crust of the earth. It is but slightly soluble in water, yet dissolves in this medium more than in any other ordinary solvent.

Although oxygen enters into combination with every element except fluorin and the members of the inactive argon group (see page 65), at ordinary temperatures it is comparatively inactive and most reactions take place so slowly as to be almost imperceptible. At higher temperatures, however, it becomes very active and it unites with many substances so rapidly that both heat and light are produced. Union with oxygen is the chemical reaction ordinarily understood by the term, combustion.

Oxygen itself does not burn under ordinary conditions, but other substances burn in it, and the presence of oxygen gives to the atmosphere its power to support combustion. As might be expected, all substances burn more rapidly in pure oxygen than in air, and the ability to hasten combustion is taken as a test for the presence of oxygen.* A piece of charcoal, glowing in the air, bursts into flame when introduced into a jar containing oxygen and many substances, such as iron, which do not burn in air, burn vigorously in pure oxygen.

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* Some of the oxids of nitrogen support combustion better than air but they may be readily differentiated from oxygen by their odors.

An *allotropic modification* of the element is known as **ozone.** It is a gas with a very characteristic penetrating odor, and pale blue color seen only in large volumes of the gas. It may be formed by subjecting the ordinary modification to the action of electricity, when a contraction in volume occurs. In general, whenever oxygen is formed, some ozone is formed also. It is comparatively unstable at ordinary temperatures and, on heating to 300°, breaks down completely into the ordinary modification with an increase in volume half as great as the original volume. For these and other reasons, the molecule of ozone is supposed to be O_3 while that of ordinary oxygen is O_2.

Ozone is about as active at ordinary temperatures as oxygen is at high temperatures. It is one of the most energetic oxidizing agents known, usually giving up only one-third of its oxygen and changing into the ordinary form. Moist ozone oxidizes all the commoner metals except gold and platinum to the highest possible valence and affects many of the non-metallic elements in the same way.

Oxids *are formed by the direct union of elements with oxygen* (or ozone) *and also by heating the corresponding hydroxids, carbonates, nitrates, or salts of organic acids* which usually decompose into carbonates first. Many oxids are insoluble in water. Of these, oxids formed by metals are soluble in the strong acids,* while those formed by non-metallic elements are soluble in solutions of the strong bases.

All oxids unite with water to form hydroxids, either directly or indirectly.

$$Na_2O + H_2O \rightarrow 2NaOH \qquad CaO + H_2O \rightarrow Ca(OH)_2$$
$$B_2O_3 + 3H_2O \rightarrow 2B(OH)_3 \qquad SiO_2 + 2H_2O \rightarrow Si(OH)_4$$
$$P_2O_5 + 5H_2O \rightarrow 2P(OH)_5 \qquad SO_3 + 3H_2O \rightarrow S(OH)_6$$

Although the properties of these hydroxids grade one into the other very gradually, for convenience they may be divided into two general classes:

(a) *Those hydroxids which in aqueous solution separate* $\overset{+}{H}$ *ions are known as* **acids,** *and the elements from which they are derived as* **non-metallic** *or* **acid-forming elements.**

(b) *Those hydroxids which in aqueous solution separate* $\overset{-}{OH}$ *ions are known as* **bases,** *and the elements from which they are derived as* **metals** *or* **base-forming elements.**

The hydroxids of certain elements do not separate $\overset{+}{H}$ or $\overset{-}{OH}$ ions to any *great* extent but, to a *slight* extent, they may separate either under different conditions, *i. e.*, they may act either as acids or as bases, depending on their environments. In the presence of more strongly acidic hydroxids, they act as bases and in the presence of distinctly basic hydroxids they play the part of acids. (See page 22.)

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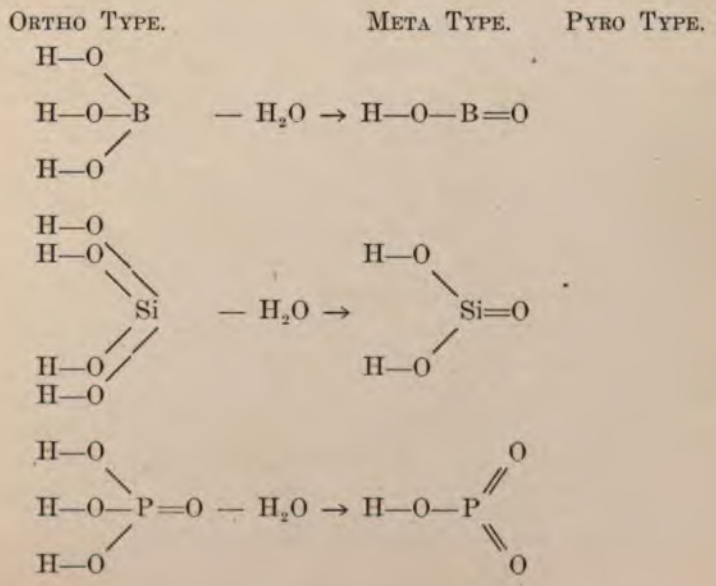
* Certain naturally-occurring oxids, or the artificial products which have been strongly ignited, are soluble with extreme difficulty.

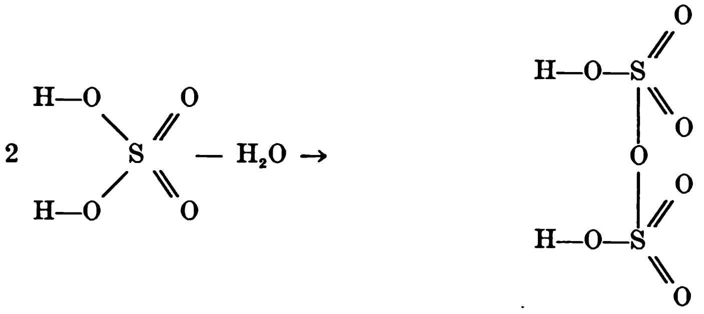
Many elements unite with oxygen in more than one proportion and *the chemical nature of* the corresponding *hydroxids varies with the state of oxidation, the more highly-oxidized compounds possessing more acidic properties than those in which the element exhibits a smaller valence* (see page 45). As the valence of the element rises, usually the full amount of water necessary to form the normal hydroxid does not unite with the oxid but the commonly-occurring forms may be represented as the normal hydroxids minus one or more molecules of water.

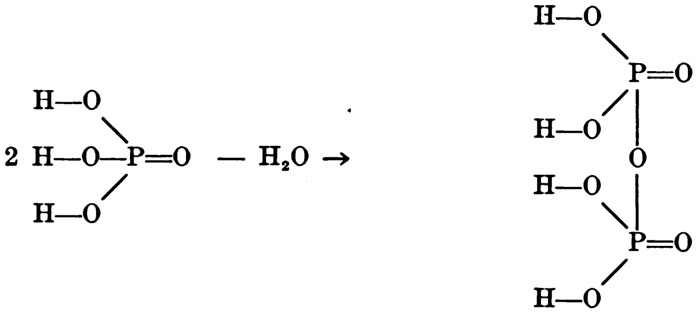
$$P(OH)_5 - H_2O \rightarrow H_3PO_4 \qquad S(OH)_6 - 2H_2O \rightarrow H_2SO_4$$

The different degrees of hydration are denoted by the prefixes ortho, meta and pyro, these terms being used most commonly in connection with acidic hydroxids. **Ortho acids** represent the ordinary degree of hydration, *i. e.*, the form most commonly-occurring. **Meta acids** are formed from ortho acids by the loss of a molecule of water. **Pyro acids** are obtained by the separation of one molecule of water from two molecules of the ortho acids.



ORTHO. PYRO.





Water, H_2O.

Water, the common oxid of hydrogen, is a clear, almost colorless, tasteless liquid, boiling at 100° and changing to a colorless solid, ice, at 0°. It dissolves a great many substances readily and is the most general solvent known. It may be regarded as the hydroxid of hydrogen and as such it dissociates to an exceedingly small degree into $\overset{+}{H}$ and $\overline{OH}$ ions.[*] It is, therefore, either acidic or basic in nature. With most bodies, it acts as a neutral reagent, however, but with substances possessing extreme properties, water takes on a definite character of its own.

In contact with the strong base-forming elements water acts as an acid. These metals show a much greater tendency to pass into the ionic condition than hydrogen does. When sodium or potassium is thrown upon water the electrical charge passes from the $\overset{+}{H}$ ions of the water to the metal, which then enters the ionic condition. On losing its charge, the hydrogen passes out of the ionic condition and is liberated in gaseous form. A comparison of the equations expressing the action of water and of hydrochloric acid on metallic sodium will show that water acts as a typical acid.

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[*] There is evidence to indicate that the dissociation of water into $\overset{+}{H}$ and $\overline{OH}$ ions is only the first step in the process and that water, like other weak acids, undergoes further dissociation to a very slight degree with the formation of $\overline{O}$ ions and a second $\overset{+}{H}$ ion.

$$\mathbf{2Na} + 2\overset{+}{\mathrm{H}} + 2\ \overset{-}{\mathrm{O}}\mathrm{H} \rightarrow 2\overset{+}{\mathrm{Na}} + 2\ \overset{-}{\mathrm{O}}\mathrm{H} + H_2$$
$$\mathbf{2Na} + 2\overset{+}{\mathrm{H}} + 2\overset{-}{\mathrm{Cl}} \rightarrow 2\overset{+}{\mathrm{Na}} + 2\overset{-}{\mathrm{Cl}} + H_2$$

Strong acid-forming elements, on the other hand, cause water to play the part of a base. Fluorin and chlorin show a much greater tendency to assume a negative charge than the hydroxyl radicle does. When these gases are passed into water, the charge passes from the hydroxyl ion of the water to the halogen, which enters the ionic condition. The hydroxyl radicles pass from the ionic condition and decompose into water and oxygen as the equation shows:

$$4F + 4\overset{+}{\mathrm{H}} + 4\ \overset{-}{\mathrm{O}}\mathrm{H} \rightarrow 4\overset{+}{\mathrm{H}} + 4\overset{-}{\mathrm{F}} + 2\mathrm{H_2O} + O_2$$

Although water dissociates to an extremely small degree (only one or two parts in a thousand million being ionized), it causes substances dissolved in it to dissociate to a greater degree than any other common solvent does (see page 13). This fact, taken in connection with the great solvent power of water, makes aqueous solution a most important medium for the investigation of chemical reactions.

Hydrogen Dioxid, Hydrogen Peroxid, H_2O_2.

Hydrogen dioxid is a colorless oily liquid, boiling at 85° under 70 mm. pressure. When heated under ordinary atmospheric pressure, it decomposes with explosive violence into water and oxygen. The liquid reacts acid to litmus and is miscible with water in all proportions, a 3 per cent. solution being the ordinary hydrogen peroxid of commerce. In solution it is much more stable than in the pure state.

Hydrogen dioxid stands in relation to water about as ozone does to oxygen. At ordinary temperatures, its solutions decompose slowly into water and oxygen and, in the presence of reducing agents, this decomposition is frequently rapid. Therefore, hydrogen peroxid is a good oxidizing agent, each molecule of peroxid giving up an atom of oxygen.

In alkaline solutions, iron, cobalt and manganese are oxidized to the trivalent condition and chromium passes from the trivalent base-forming condition into the hexavalent acid-forming condition. Cobaltic oxid, Co_2O_3, and manganese dioxid decomposes hydrogen peroxid very rapidly and cause an abundant evolution of oxygen.

In acid solutions, chromium is oxidized one step higher than in alkaline solutions and becomes the blue heptavalent perchromic acid (see page 192). This reaction is frequently used as a test for hydrogen dioxid although this reagent is less delicate and less reliable than titanium sulfate for the detection of H_2O_2. In this latter test, the colorless tetravalent salt of titanium is oxidized to the hexavalent condition, which is characterized by a yellow or orange color. (See page 306.)

Although a typical oxidizing agent, hydrogen dioxid, because of its instability, reacts with certain other oxidizing agents in such a way that both are reduced and oxygen gas liberated. For this reason, permanganate is bleached according to the equation:

$$5H_2O_2 + 2HMnO_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + 8H_2O + 5O_2$$

Similarly hypochlorous acid is reduced to hydrochloric acid and perchromic acid is reduced to trivalent chromium by an excess of hydrogen peroxid (see page 267). In alkaline solutions, also, copper, silver and gold salts are reduced to the metals and oxygen is evolved.

The **salts of hydrogen dioxid** are the metallic dioxids or peroxids. Only a few are known. Of these, the peroxids of the alkali metals only are readily soluble; the peroxids of the alkaline earths are much less soluble and others are highly insoluble.

Sodium peroxid, Na_2O_2, is a heavy straw-colored powder which unites with water to form a hydrate, $Na_2O_2.8H_2O$, so energetically that much heat is liberated. It is hydrolyzed considerably, however, so that its solution in water is equivalent to an alkaline solution of H_2O_2. It is used as a very strong oxidizing agent.

Barium dioxid, BaO_2, treated with acids, is the source of commercial hydrogen peroxid.

$$\mathbf{BaO_2} + H_2SO_4 \rightarrow \mathbf{BaSO_4} + H_2O_2$$

Manganese dioxid, MnO_2, and **lead dioxid, PbO_2,** are typical higher oxids. When warmed with hydrochloric acid, their equivalent of oxygen is used in oxidizing the acid, and chlorin, instead of oxygen, is liberated.

$$\mathbf{MnO_2} + 4HCl \rightarrow MnCl_2 + 2H_2O + \mathit{Cl_2}$$

The **barium ion, $\overset{++}{Ba}$,** causes no precipitate, for Ba_2O_2, although quite insoluble, is not formed in the "wet way."

The **silver ion, $\overset{+}{Ag}$,** causes no precipitate, for Ag_2O_2 is not formed in the "wet way."

SULFUR. S — 32.1.

The element **sulfur** exists in several modifications. The ordinary form consists of a light yellow, crystalline substance melting at 114.5° to an amber fluid, which becomes darker and more viscous as the temperature rises to 250°. On higher heating, it becomes mobile again and boils at 450°. It is not dissolved appreciably in ordinary solvents, but is readily soluble in 2 or 3 parts of carbon disulfid. Another modification of different crystal form, also soluble in CS_2, is known. It is stable only above 95°. At least two amorphous forms are recognized, one soluble in CS_2; the other, "plastic sulfur," is elastic and insoluble in CS_2. Sulfur precipitated by the decomposition of sulfur-containing compounds is generally soluble in CS_2. "Flowers of sulfur" is a finely divided form obtained by rapid cooling of the vapor. It is partly soluble and partly insoluble in CS_2.

All modifications of sulfur afford for the most part the same chemical reactions. They dissolve in warm solutions of alkaline hydroxids, sulfids and sulfites, entering into chemical reactions in each case, according to the equations:

$$6NaOH + 4\mathbf{S} \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$$
$$xNa_2S + x\mathbf{S} \rightarrow Na_2S_2,\ Na_2S_3,\ Na_2S_4,\ Na_2S_5$$
$$Na_2SO_3 + \mathbf{S} \rightarrow Na_2S_2O_3$$

Sulfur unites directly with most elements, generally requiring temperatures higher than ordinary for appreciable reaction.

Sulfur burns with a pale blue flame to **sulfur dioxid, SO_2**, a colorless gas (B. P. —8°) with a very sharp, pungent odor, used as a disinfectant and bleaching agent. It is the anhydrid of sulfurous acid. More than forty volumes of the gas dissolve in one volume of water, all of which may be removed again on boiling the solution. It oxidizes slowly in the air at ordinary temperatures, more rapidly when heated or in the presence of oxidizing agents, to SO_3.

Sulfur trioxid exists in two different forms. One modification is a liquid,—M. P. 15°; B. P. 46°—which changes, on standing, into a white, crystalline solid which sublimes without melting. As produced in the laboratory usually, SO_3 appears as heavy white fumes without particular odor which produce violent coughing when inhaled. It is the anhydrid of sulfuric acd.

Free sulfur is usually detected by burning it to SO_2, which may be recognized readily by its odor, or the oxidation product may be collected in water and detected by any of the tests for sulfurous acid. In organic bodies which do not ionize, sulfur is detected by converting it into compounds which dissociate into some one of the well-known ions containing sulfur. (See pages 308 and 309.)

The simple **sulfur ion, $\overset{=}{S}$,** may be considered as the anion of the acid, H_2S. United with oxygen, sulfur forms several important ions which will be considered under their corresponding acids.

Hydrosulfuric Acid, Hydrogen Sulfid, H_2S.

Hydrogen sulfid is a colorless gas with a very characteristic disagreeable odor like that of decaying eggs. It acts as a poison on the human system, dilute chlorin being the best antidote. It burns with a pale blue flame to water and SO_2. At ordinary temperatures, it oxidizes readily, either to water and free sulfur, or to H_2SO_4 as the final product. Therefore, it is a strong reducing agent, each molecule of H_2S absorbing either one or four atoms of oxygen. It is fairly soluble in water (2 or 3 volumes of gas in one of water), its solution being known in the laboratory as "hydrogen sulfid water" and, when occurring in nature, as "sulfur water." By boiling the solution, all H_2S may be removed.

Hydrogen sulfid in aqueous solution acts as a very weak acid, dissociating *slightly* according to the first equation and to an *extremely small degree* according to the second equation.

$$(1)\quad H_2S \rightarrow \overset{+}{H} + H\overset{-}{S} \qquad\qquad (2)\quad H\overset{-}{S} \rightarrow \overset{+}{H} + \overset{=}{S}$$

Consequently there are always more $H\overset{-}{S}$ than $\overset{=}{S}$ ions in its solutions, but, since acid salts are much more soluble than normal salts, the normal sulfids are precipitated from solutions. The sulfids of the alkali metals are soluble and suffer hydrolysis. The sulfids of the akaline earth metals are fairly insoluble, but, in the presence of water, are changed by hydrolysis into acid sulfids which are readily soluble. The sulfids of magnesium, aluminum, chromium and ferric iron are soluble, but, owing to the fact that the hydroxids of these metals are insoluble, the sulfids are completely hydrolyzed in the presence of water and the hydroxids are precipitated. The sulfids of cobalt, nickel,* manganese, zinc and ferrous iron, though insoluble in water, are soluble in the stronger acids and hence are not precipitated in the presence of HCl. The sulfids of silver, mercury, lead, copper, bismuth, cadmium, arsenic, antimony, tin, gold and platinum are precipitated in the presence of dilute HCl, but of these the sulfids of lead, cadmium, antimony and tin are soluble in more concentrated acid, while the others do not dissolve in HCl at all, contrary to the general rule that salts or weaker acids dissolve in solutions of stronger acids (see page 35). The varying action of H_2S on salts of the various metals is taken advantage of in qualitative analysis and is the basis of the separation into groups. (See page 248.)

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* For the peculiar action of CoS and NiS toward HCl see pages 229 and 233.

The differing action of HCl, or the $\overset{+}{H}$ ion in general, on these different sulfids depends principally on the relative solubilities of these sulfids in water. Those which are highly insoluble in water are not soluble in HCl, while those which are most soluble in water dissolve most readily in HCl. To illustrate: When H_2S is passed into a solution of a soluble copper salt acidified with HCl, there are present $\overset{++}{Cu}$, $\overset{=}{S}$ and $\overset{+}{H}$ ions. Two distinct conditions of equilibrium will exist in the solution (see page 24), one with regard to CuS, another with regard to H_2S. In each there will be one common term, the $\overset{=}{S}$ ion. Hydrogen sulfid is quite soluble and the solution may be saturated with the gas and a definite equilibrium obtained between the dissolved but undissociated H_2S and the ions $\overset{+}{H}$ and $\overset{=}{S}$. Since H_2S is weakly acidic, the concentration of the ions will be represented by small factors, while that representing the undissociated substance will be relatively large. Should the concentration of $\overset{+}{H}$ and $\overset{=}{S}$ ions become greater than is necessary for the stated condition of equilibrium, undissociated H_2S will be formed, the solution will become supersaturated and the gas will bubble out.

On the other hand, *copper sulfid* is extremely insoluble in H_2O, hence only very small concentrations of $\overset{++}{Cu}$ and $\overset{=}{S}$ ions can exist in the solution together. There is, however, a high concentration of $\overset{++}{Cu}$ due to the original soluble copper salt. When H_2S is introduced, the concentration of sulfid ions becomes too great for equilibrium. Undissociated CuS is formed in such quantities that the solution becomes supersaturated and precipitates CuS long before it becomes saturated with H_2S.

Conversely CuS does not dissolve even in concentrated HCl, for the concentration of $\overset{=}{S}$ ions necessary to separate CuS from solution is less than that required to separate H_2S. Therefore a saturated solution of CuS never contains $\overset{=}{S}$ ions in sufficient quantity to separate H_2S.

Cadmium sulfid is considerably more soluble than CuS, hence requires a higher concentration of $\overset{=}{S}$ ions to precipitate it from solution than does CuS. With the increased concentration of $\overset{=}{S}$ ions, a lower concentration of $\overset{+}{H}$ will be sufficient to cause the separation of H_2S from solution. Nevertheless the concentration of $\overset{+}{H}$ ions given by dilute HCl is not sufficiently great to cause the separation of H_2S rather than CdS. Therefore, CdS is precipitated from solutions of cadmium salts by H_2S in the presence of not more than 4 per cent. of HCl. If the concentration of HCl be greater than this, CdS is not precipitated. On the other hand, CdS is dissolved readily by concentrated HCl, for the concentration of $\overset{=}{S}$ ions given by a saturated solution of CdS is greater than is necessary for equilibrium with regard to the H_2S. Undissociated H_2S is formed, the solution becomes supersaturated and the gas bubbles out. By this decrease in the concentration of the $\overset{=}{S}$ ion, the equilibrium with regard to CdS is disturbed and more CdS goes into solution to restore the concentration of $\overset{=}{S}$ ions. This causes further liberation of H_2S which, in turn, causes further solution of CdS.

Zinc sulfid is more soluble than CdS, hence requires a higher concentration of $\overset{=}{S}$ ions to cause its precipitation from solution. But with the increased concentration of $\overset{=}{S}$ ions, a correspondingly smaller concentration of $\overset{+}{H}$ ions will be sufficient to cause the separation of H_2S. The conditions necessary to separate ZnS differ but little from those necessary to separate H_2S. The concentration of $\overset{+}{H}$ ions given by HCl is sufficiently great to exceed the equilibrium conditions for H_2S before those for ZnS are reached. Hence, ZnS cannot be precipitated in the presence of HCl. But, on the contrary, ZnS dissolves readily in dilute HCl; for the concentration of $\overset{=}{S}$ ions given by a saturated solution of ZnS is sufficiently great to cause the separation of H_2S.

The concentration of $\overset{+}{H}$ ions given by acetic acid, however, is much less than that furnished by HCl. If H_2S is passed into a zinc solution slightly acidified with acetic acid, the concentration of $\overset{=}{S}$ ions necessary to precipitate ZnS will be reached before it becomes great enough to separate H_2S; *i. e.,* before the solution becomes saturated with H_2S. Therefore, ZnS is precipitated and, once thrown down, it does not dissolve in acetic acid.

Ferrous sulfid is still more soluble than ZnS and it cannot be precipitated in the presence of acetic acid, for a saturated solution of H_2S does not contain sufficient $\overset{=}{S}$ ions to cause the separation of FeS. The alkaline sulfids are much more soluble than H_2S, however, and their solutions afford $\overset{=}{S}$ ions in sufficient quantity to cause the separation of FeS.

Conversely, FeS will dissolve in acids readily, for its saturated solution contains sufficient $\overset{=}{S}$ ions to cause the separation of H_2S. In the laboratory, H_2S is generally prepared by the action of acid on FeS, this sulfid being used because of its cheapness.

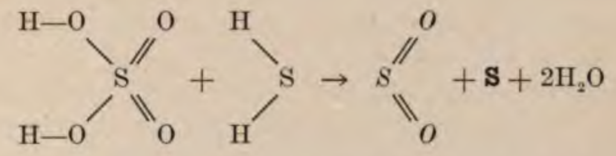
Sodium sulfid is exceedingly soluble. Its solutions contain very high concentrations of $\overset{=}{S}$ ions, so great, in fact, that the concentration of $\overset{+}{H}$

ions due to dissociated water is sufficiently great to exceed the equilibrium for H_2S and cause some of the undissociated substance to form, the odor of which may be detected in the solution. This constitutes the hydrolysis of soluble sulfids.

These facts may be summarized and tabulated in the following manner. The condition represented is that equilibrium for H_2S already discussed, in which any increase in the concentration of $\overset{+}{H}$ or of $\overline{S}$ ions will cause the separation of H_2S from solution. The large letters represent high concentrations, small letters correspondingly low concentrations.

Salt.	Solubility.	Concentration of $\overline{S}$ ions.	Concentration of $\overset{+}{H}$ ions.	
Na_2S	decreasing ↓	S	H	From water
FeS		S	H	From acetic acid
ZnS		S	H	From very dil. HCl
CdS		S	H	From 4 per cent. HCl
CuS		s	H	No acid gives sufficient $\overset{+}{H}$ ions

Sulfids, not soluble in HCl, may be decomposed by heating with concentrated H_2SO_4. The H_2S set free is oxidized by the hot H_2SO_4, however, into water and free sulfur; and SO_2, from the reduction of H_2SO_4, is given off instead of H_2S.



Sulfur may be detected in sulfids of this character by fusing with NaOH, when transposition takes place. Much of the Na_2S formed will be oxidized during the fusion, but sufficient will remain in the aqueous extract to give reactions for the sulfid ion.

On ignition out of contact with the air, most sulfids fuse unchanged. When heated in the atmosphere, the sulfur frequently burns out, leaving an oxid, or the sulfid may be oxidized to a sulfate.

All sulfids formed by precipitation are transposed by boiling with Na_2CO_3.

The **barium ion, $\overset{++}{Ba}$,** gives no precipitate with solutions containing sulfids under ordinary conditions, for, although BaS is somewhat insoluble, it hydrolyzes to BaSH, and then to $Ba(OH)_2$ and H_2S, all of which are soluble.

The **silver ion, $\overset{+}{Ag}$,** precipitates black Ag_2S, insoluble in most of the ordinary reagents. Hot HNO_3 oxidizes it to the soluble Ag_2SO_4 and a large excess of warm KCN will dissolve it, forming $KAgC_2N_2$ and K_2S.

The **lead ion, $\overset{++}{Pb}$,** precipitates black PbS, soluble in concentrated HCl and in dilute HNO_3 on warming. A filter-paper moistened with lead acetate is often used to detect fumes of H_2S, but sodium plumbite, Na_2PbO_2, is a more delicate reagent for the same purpose. It may be prepared by adding NaOH or KOH to a soluble lead salt until the $Pb(OH)_2$ first precipitated is redissolved.

Sodium nitro-ferricyanid, or **nitroprussid, $Na_2(Fe\equiv C_5N_5NO)$,** produces a transient purple color in alkaline solutions of sulfids but not in acid or neutral solutions.

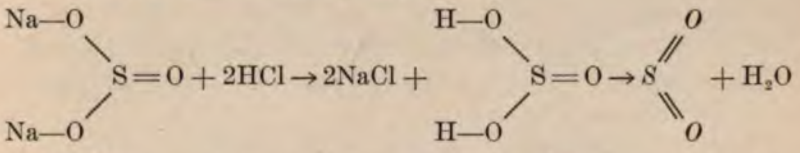
Metallic silver, also copper and mercury, are blackened by the action of H_2S or alkaline sulfids in the presence of water and oxygen (air) according to the equation:

$$\mathbf{4Ag} + 2Na_2S + O_2 + 2H_2O \rightarrow \mathbf{2Ag_2S} + 4NaOH$$

A solution of H_2S in water becomes turbid on standing, owing to oxidation and separation of free sulfur, as has been stated previously. Under similar conditions, an alkaline sulfid does not become turbid, although oxidation takes place in the same way. The sulfur set free by the action of oxygen reacts with the alkaline sulfid to form **polysulfids,** of which the following types are known, Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5. The acids corresponding to these salts are very unstable and, on acidifying a solution of a polysulfid, H_2S is liberated and free sulfur precipitated for the most part. Under appropriate conditions, however, a yellow oil may be obtained which consists of hydrogen and sulfur in the proportions corresponding to a mixture of the hydrogen polysulfids. It soon decomposes into H_2S and sulfur. The alkaline polysulfids are important in analysis. See pages 252 and 253.

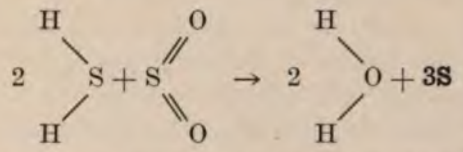
Sulfurous Acid, H_2SO_3.

When sulfur dioxid is passed into water, the gas is absorbed and the solution becomes acid, owing to an interaction between the gas and the water to form a compound known as sulfurous acid. Only a small portion of the gas is actually united chemically with the water and in any solution the condition of equilibrium is one in which a large proportion of the SO_2 is simply dissolved in the solvent. This is indicated by the fact that, on boiling or evaporating the solution spontaneously, just in proportion as the gas is removed, the sulfurous acid is decomposed into its anhydrid, SO_2, and these reactions continue simultaneously until finally nothing but water remains. Inasmuch as sulfurous acid cannot be isolated, its formula is not known with certainty but it probably is H_2SO_3. It acts as a weak dibasic acid, forming salts which are fairly stable. On the addition of an acid to a sulfite, however, sulfur dioxid is liberated for the reasons already set forth.



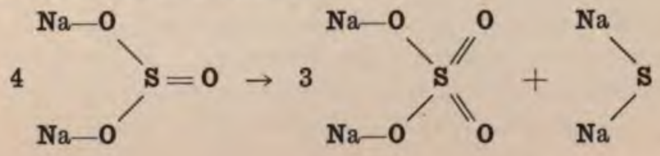
All sulfites are strong reducing agents, absorbing one atom of oxygen for each molecule of sulfite, forming sulfates. Iodin, bromin and permanganate are bleached at once and other oxidizing agents quickly reduced. Mercurous salts are unaffected in the cold but, on boiling, are reduced by sulfurous acid exactly as with stannous chlorid. At ordinary temperatures atmospheric oxygen causes a slow oxidation, especially in solutions, hence all sulfites contain some sulfate.

Strong reducing agents, on the other hand, cause sulfurous acid to act as an oxidizing agent. Under the influence of nascent hydrogen it is reduced, first to hyposulfurous acid, $H_2S_2O_4$, a weak acid with strong reducing properties. The final product of the reduction is H_2S. Hydrogen sulfid reduces sulfurous acid and its anhydrid according to the equation:



Sulfites and other oxidized compounds of sulfur are reduced to sulfids by heating with charcoal.

Heated *out of contact with the air,* sulfites generally decompose into SO_2 and metallic oxids. Alkaline sulfites, under the same circumstances, decompose according to the equation:



Heated *in the air*, however, sulfates are generally formed.

All normal sulfites are insoluble or soluble with difficulty in water, with the exception of the salts of the alkali metals. All acid sulfites are soluble. In the stronger acids, all sulfites dissolve with readiness.

All sulfites are transposed by boiling with Na_2CO_3.

The **barium ion, $\overset{++}{\mathbf{Ba}}$,** precipitates white granular $BaSO_3$ from neutral or alkaline solutions containing the $\overset{-}{SO}_3$ ion. It is readily soluble in dilute HCl and will not precipitate in the presence of acetic acid (distinction from $BaSO_4$).

The **silver ion, $\overset{+}{\mathbf{Ag}}$,** precipitates white granular Ag_2SO_3, which, on boiling, precipitates dark gray metallic silver according to the equation:

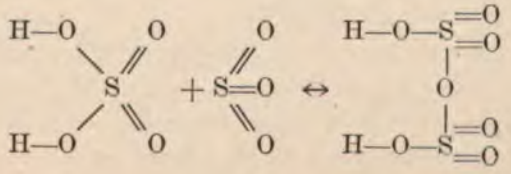
$$\mathbf{2Ag_2SO_3} \rightarrow Ag_2SO_4 + SO_2 + \mathbf{2Ag}$$

Silver sulfite is soluble in dilute HNO_3, like all sulfites, and in NH_4OH, like most silver salts. It dissolves in solutions of alkaline sulfites, forming the soluble salt, $AgNaSO_3$.

Sulfuric Acid, H_2SO_4.

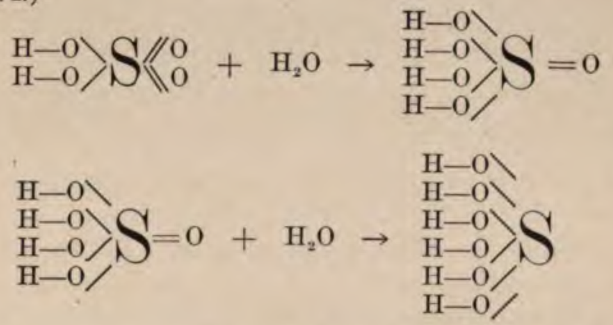
Pure sulfuric acid is a colorless, oily liquid at ordinary temperatures but, on cooling, solidifies to a white crystalline body, melting at 10.5°. When heated, it decomposes somewhat into its anhydrid, SO_3 and water, and it boils at 338°. The distillate is not pure H_2SO_4, however, for it contains about 1.5 per cent. of water formed during the heating, for the anhydrid and the water do not unite completely again on cooling. The product obtained by distillation has a specific gravity of 1.84 and contains about 98.5 per cent. H_2SO_4. Commercial acid, which is not distilled but is obtained from a dilute acid by heating to drive off as much of the water as possible, contains only 93–96 per cent. H_2SO_4. The product obtained by either process is known as **concentrated sulfuric acid.**

Fuming sulfuric acid consists of concentrated sulfuric acid in which the anhydrid, SO_3, has been dissolved. From it, at low temperatures, pyro-sulfuric acid, $H_2S_2O_7$, can be crystallized but this decomposes into H_2SO_4 and SO_3 on warming.



Fuming sulfuric acid has a greater decomposing action than concentrated sulfuric acid because of the anhydrid it contains.

When **concentrated sulfuric acid** is mixed with water, a decided rise in temperature is noted due to the formation of two hydrates, $H_2SO_4.H_2O$ and $H_2SO_4.2H_2O$. These hydrates probably are the normal hexahydroxid of sulfur and its first dehydration product, as the equations show: (See page 174.)



Because of this reaction, concentrated sulfuric acid absorbs water vapor very readily and holds it firmly, hence it is much used as a drying agent.

Sulfuric acid is the strongest of the common dibasic acids, dissociating in steps according to the rule for polybasic acids:

$$(1)\ H_2SO_4 \rightarrow \overset{+}{H} + H\overset{-}{SO}_4 \qquad (2)\ H\overset{-}{SO}_4 \rightarrow \overset{+}{H} + \overset{=}{SO}_4$$

In a solution of ordinary dilution, the second step of the reaction takes place to about the same extent as the first step, so that the prevalent ion is $\overset{=}{SO}_4$ and not $H\overset{-}{SO}_4$.

In dilute solution H_2SO_4 acts simply as an acid but *hot concentrated sulfuric acid is an oxidizing agent,* being readily reduced to sulfurous acid which decomposes with the liberation of SO_2 and water. When heated with Na_2CO_3 on charcoal, sulfates, and other oxidized compounds containing sulfur, are reduced to sulfids. A similar reduction of sulfates to sulfids takes place in natural waters under the influence of organic matter and certain bacteria and is one of the sources of "sulfur water," (H_2S).

On ignition, sulfates of the alkali metals fuse unchanged, other sulfates are more or less decomposed into the anhydrid and metallic oxids while the salts of barium, strontium, calcium and lead are practically unchanged. Acid sulfates break down readily, first into pyro-sulfates and, finally, into normal sulfates with the liberation of the anhydrid in the nascent condition.

$$\mathbf{2HNaSO_4} \rightarrow H_2O + \mathbf{Na_2S_2O_7} \rightarrow \mathbf{Na_2SO_4} + SO_3$$

Nascent sulfur trioxid formed in this way is particularly effective in decomposing silicates and oxids insoluble in acids. *Fusion with acid potassium sulfate* is often a satisfactory means of obtaining a refractory substance in soluble form. (See page 242.)

Sulfates *are generally soluble in water,* the exceptions being $BaSO_4$, $SrSO_4$, $CaSO_4$ and $PbSO_4$. These compounds, being salts of a strong acid, do not dissolve to any great extent in solutions of the stronger acids, HCl or HNO_3.

Several soluble sulfates separate from aqueous solution in the same crystal form, each taking up seven molecules of water of crystallization. These compounds are known as "vitriols," a term derived from the older name of sulfuric acid, "oil of vitriol." The sulfates of ferrous iron, zinc, magnesium, cadmium, cobalt, nickel, manganese and copper are the best known of the "vitriols."

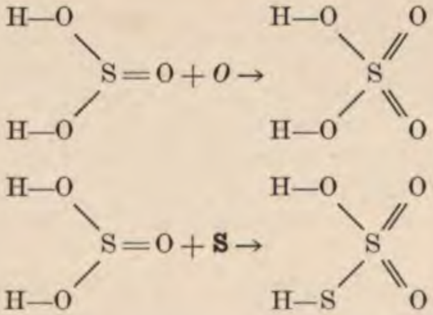
All sulfates are transposed by boiling with Na_2CO_3, with the exception of $BaSO_4$, which requires fusion with the same reagent (see page 99).

The **barium ion, $\overset{++}{\textbf{Ba}}$,** added to solutions containing the $\overset{=}{\text{SO}}_4$ ion, precipitates white crystalline $BaSO_4$, practically insoluble in all solvents.

The **silver ion, $\overset{+}{\textbf{Ag}}$,** gives no precipitate, except in very concentrated solutions when white Ag_2SO_4 falls.

Thiosulfuric Acid, $H_2S_2O_3$.

Just as H_2SO_3 is oxidized by oxygen to H_2SO_4, so H_2SO_3 may be oxidized by sulfur to $H_2S_2O_3$, thiosulfuric acid.



Although **thiosulfuric acid** corresponds in its degree of oxidation to sulfuric acid, the presence of the second sulfur atom in the molecule makes it resemble sulfurous acid far more than sulfuric acid. While a whole series of salts are well known, the acid itself is entirely unknown, for it is quite as unstable as sulfurous acid and, when set free from one of its salts, it decomposes into SO_2, water and free sulfur, the precipitation of the latter element serving to distinguish thiosulfates from sulfites. The similarity of decomposition products would naturally suggest a similarity in chemical properties and thiosulfuric acid proves to be a vigorous reducing agent. Strong oxidizing agents, such as chlorin and bromin, change it immediately into sulfuric acid with or without a partial liberation of sulfur. Hence the amount of oxygen taken up by the thiosulfate will vary under different conditions. The milder oxidizing agents, such as iodin, do not carry the oxidation as far as H_2SO_4, as the equation shows:

$$2H_2S_2O_3 + 2I \rightarrow H_2S_4O_6 + 2HI$$

Tetrathionic acid, $H_2S_4O_6$, is one of a series of **polythionic acids** of which the following members are known: $H_2S_2O_6$, $H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$. They are all strong but quite unstable acids, readily oxidizing to sulfuric acid. Tetrathionic acid is oxidized by bromin or other strong oxidizing agent to H_2SO_4 according to the equation:

$$H_2S_4O_6 + 14Br + 10H_2O \rightarrow 4H_2SO_4 + 14HBr$$

The barium salt of tetrathionic acid is soluble, hence this acid may be differentiated from sulfuric acid.

Thiosulfuric acid reduces ferric salts to the ferrous condition and cupric salts to the cuprous condition. Cuprous salts are generally insoluble, but a soluble complex sodium-cuprous thiosulfate is formed in this case by an excess of an alkaline thiosulfate.

Salts of thiosulfuric acid are much more stable than the free acid, but, on heating, they break down analogously to sulfites, the excess of sulfur appearing as a sublimate in closed-tube reactions:

$$\mathbf{4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S + 4S}$$

Heated with Na_2CO_3 on charcoal, thiosulfates are reduced to sulfids, like other oxidized sulfur compounds.

All thiosulfates dissolve in water, only the barium, lead and silver salts being soluble with difficulty.

All thiosulfates are transposed by boiling with Na_2CO_3.

Thiosulfuric acid appears to be a much stronger acid than sulfurous acid. Its salts, of which the most important is the "hypo" of photographers, $Na_2S_2O_3.5H_2O$, separate the ion, $\overset{=}{S_2O_3}$, with readiness, but, in the presence of $\overset{+}{H}$ ions, it is unstable and decomposes into the ion $\overset{=}{SO_3}$ and free sulfur. Thiosulfates show a strong tendency toward the formation of complex ions with several metals, as is shown by the formation of soluble complex salts, which do not give reactions for the heavy metal present. Of these, the complex sodium-silver thiosulfate is most important because of its application in photography. See later.

The **barium ion, $\overset{++}{Ba}$,** precipitates white BaS_2O_3 from concentrated solutions only, since it is soluble in 480 parts of water.

The **silver ion, $\overset{+}{Ag}$,** if present in the correct proportion, will precipitate white $Ag_2S_2O_3$. This dissolves in an excess of an alkaline thiosulfate, forming $NaAgS_2O_3$, which is quite soluble. The latter salt unites with more alkaline thiosulfate to form the salt $Na_4Ag_2(S_2O_3)_3$, which is exceedingly soluble, and in solution gives practically no $\overset{+}{Ag}$ ions. In acid solution, on boiling, this complex salt decomposes and silver sulfid is precipitated.

Persulfuric acid, $H_2S_2O_8$, is an unstable compound containing heptavalent sulfur. Its salts are much better known than the acid. They act as strong oxidizing agents, taking up water and decomposing readily into H_2SO_4 and nascent oxygen.

Group 6, Second Type.

Chromium 52.1; Molybdenum 96; Tungsten 184; Uranium 238.5.

The compounds formed by the elements belonging to this second type resemble closely those of the preceding type, but these free elements are decidedly more metallic than the former, being characterized by brilliant lustre, high specific gravity and good conductivity of heat and electricity. Hydrids are unknown or unimportant. Each element forms several oxids and hydroxids. Of the latter, those in which the valence of the element is low (two or three), possess weakly basic properties, while those in which the characteristic valence of six, or a higher valence, is shown, are acids of considerable strength.

Chromium is the most commonly-occurring and, as a type of the other members of the group, will be considered in detail.

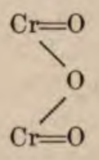
CHROMIUM. Cr — 52.1.

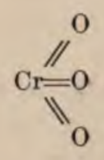
Chromium is a difficultly fusible, gray-white, crystalline metal. It is not changed by air or water at ordinary temperatures but, when heated, burns to the green oxid, Cr_2O_3. The metal is very infrequently met with. since it is only with difficulty reduced from its compounds.

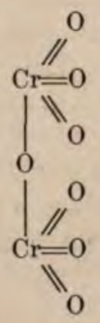
Chromium dissolves fairly well in dilute HCl and H_2SO_4. Concentrated acids in general, and HNO_3 even when dilute have but little effect; for the metal enters the "passive" condition in which it is not dissolved by these reagents. Much energy is liberated when the element passes into the ionic condition, hence no other metal will precipitate chromium from solutions of its salts and it is only at very high temperatures that it can be reduced in the "dry way."

Chromium forms two well-known series of compounds, the trivalent and the hexavalent, and also two other series which are less familiar, the divalent and the heptavalent. These compounds may be considered as derived from four oxids of which the first and fourth are not known with certainty.

$\mathrm{Cr{=}O}$

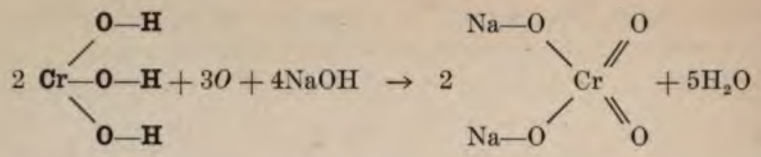






Divalent chromium acts as a fairly strong base-forming element. Bodies of this nature may be formed by the action of the strongest reducing agent, *i. e.*, nascent hydrogen, on compounds in which the element shows a higher valence. Precautions must be taken to exclude the atmosphere entirely, for on exposure to the air, they oxidize almost instantly to the trivalent condition. Hence they are very seldom encountered and will not be further considered.

Trivalent chromium acts as a weak base-forming element. Its compounds are all of a green or violet color. All of the salts hydrolyze decidedly, several of the common ones being soluble. In neutral or acid solutions they are stable, but, in alkaline solution, they slowly take up oxygen and pass into the hexavalent conditions, the transition being indicated by a change in color from green to yellow or orange. Under the influence of oxidizing agents, this change is accomplished very readily, taking place more rapidly in alkaline than in acid solutions. Sodium peroxid, Na_2O_2, is an especially satisfactory oxidizing agent in the "wet way," and KNO_3 in the "dry way." A typical equation might be written:



Hexavalent chromium forms compounds of the type K_2CrO_4 in which chromium plays the part of an acid-forming element. Compounds of this class are highly colored, either yellow or reddish. They are generally very stable, but in acid solutions and in the presence of reducing agents (alcohol is especially satisfactory), they act as strong oxidizing agents (see page 43), parting with their oxygen and breaking down into the trivalent base-forming condition. Strong ignition is alone sufficient to decompose many compounds of acidic chromium into basic compounds with the liberation of oxygen. This transition is marked by a change in color from yellow or red to green.

Heptavalent chromium acts as a strong acid-forming element. Hydrogen peroxid, acting on acid solutions of hexavalent chromium, gives rise to a deep blue color which is thought to be due to a heptavalent chromium compound of the type, $HCrO_4$, known as perchromic acid. Chromium compounds, in which the element shows a valence of seven, are exceedingly unstable and but little is known definitely in regard to them.

Heated with Na_2CO_3 and KNO_3, all chromium compounds are oxidized to Na_2CrO_4, forming a yellow melt, readily soluble in water. After acidifying slightly with $H(C_2H_3O_2)$, a drop of $AgNO_3$ produces a red precipitate. This affords a very delicate test for chromium.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all chromium compounds are brought into the trivalent condition and leave a greenish residue, Cr_2O_3.

Heated in a **borax bead,** or sodium meta-phosphate bead, all chromium compounds produce a green color.

The important **ions of chromium** are the kathion, $\overset{+++}{Cr}$, and the anions $\overset{=}{Cr}O_4$ and $\overset{=}{Cr}_2O_7$.

The Chromic Kathion, $\overset{+++}{Cr}$.

For the reactions of the chromium ion, $\overset{+++}{Cr}$, solutions of the nitrate $Cr(NO_3)_3.9H_2O$ serve best. It is a very soluble salt and will melt in its own water of crystallization at temperatures but little above the ordinary.

The **hydroxyl ion, $\overset{-}{O}H$,** precipitates gelatinous, gray-green CrO_3H_3, a substance somewhat inclined to form pseudo-solutions. On standing, more readily on heating, it loses water, forming, finally, green Cr_2O_3. This substance, when heated, becomes very resistant to acids and requires fusion with acid sulfates or with Na_2CO_3 and KNO_3 to get it into soluble form.

Chromium hydroxid acts as a weak base, dissolving in acids to form solutions containing the ion, $\overset{+++}{Cr}$, or it may act as a weak acid and dissolve in strong alkalies to form solutions containing the chromite ion, $\overset{\equiv}{Cr}O_3$. In NaOH or KOH, such action takes place. Salts of the ortho type, Na_3CrO_3, and of the meta type, $NaCrO_2$, are recognized. On boiling a solution of an alkaline chromite, hydrolysis and partial dehydration of the chromous acid, *i. e.*, the chromium hydroxid, takes place, resulting in the precipitation of this compound. In this respect, chromium differs from aluminum; for aluminum hydroxid is not precipitated on boiling a solution of alkaline aluminates (except ammonium aluminate). Ferrous meta-chromite, $Fe(CrO_2)_2$, is the ordinary "chrome iron ore," from the fusion of which with Na_2CO_3 and KNO_3, all salts of chromium are derived.

Chromium hydroxid is appreciably soluble in NH_4OH, forming, not ammonium chromite, but a complex ion, $\overset{+++}{Cr}.(NH_3)_4$.

Like aluminum and ferric hydroxids, in the presence of organic matter chromium hydroxid is partially held up and prevented from precipitating.

The **carbonate ion, $\overset{=}{\mathbf{CO}}_3$,** from solutions of alkaline carbonates, precipitates $Cr(OH)_3$.

The **sulfid ion, $\overset{=}{\mathbf{S}}$,** in acid solutions does not cause a precipitate, for Cr_2S_3, formed only in the "dry way," is soluble in acids and is hydrolyzed completely by water. By solutions of alkaline sulfids, $Cr(OH)_3$ is precipitated.

The **sulfate ion, $\overset{=}{\mathbf{SO}}_4$,** causes no precipitate, for $Cr_2(SO_4)_3.15H_2O$ is very soluble. Like aluminum, it forms double salts, known as "chrome alums," with the sulfates of univalent metals. Potassium chrome alum, $Cr_2(SO_4)_3.K_2SO_4.24H_2O$, or better $KCr(SO_4)_2.12H_2O$, is a stable violet-colored salt, soluble in 6 or 7 parts of water. Any complex ions which may exist in highly concentrated solutions are very unstable and, in dilute solutions, only the $\overset{+++}{Cr}$ and other simple $\overset{+}{K}$ and $\overset{=}{SO}_4$ ions are present.

Two modifications of many soluble chromium salts are recognized. A series of violet-colored salts exist, from the solutions of which all the metal and all the acid can be precipitated by the ordinary reagents, thus showing that the regular ions are present. By heating the violet salt, a green modification is formed, from solutions of which only a fraction of the metal and acid can be precipitated by the ordinary reagents. This indicates the formation of complex ions from the simple ions, apparently by some sort of "doubling up" process.

The **chlorid ion, $\bar{\mathrm{C}}\mathrm{l}$,** produces no precipitate, for green $\mathrm{CrCl_3.6H_2O}$ is very soluble, as are all the other halids of chromium. It is an interesting fact that on driving off the water of crystallization from this green salt, it turns violet as it dehydrates and becomes almost absolutely insoluble in water.

The **cyanid ion, $\bar{\mathrm{C}}\mathrm{N}$,** precipitates $\mathrm{Cr(OH)_3}$.

The **phosphate ion, $\bar{\mathrm{P}}\mathrm{O}_4$,** precipitates gray-green $\mathrm{CrPO_4}$, soluble in dilute mineral acids but not in acetic acid. In this respect, it resembles aluminum and ferric phosphates.

The **acetate ion, ($\mathrm{C_2\bar{H}_3O_2}$),** produces no precipitate, as $\mathrm{Cr(C_2H_3C_2)_3}$ is soluble. Whether or not chromium forms a basic acetate, like aluminum and ferric iron, is undecided. If a solution of chromium acetate is boiled by itself, no precipitate forms. If considerable ferric acetate be present, the chromium is found practically completely precipitated in some form along with the basic ferric acetate. It is necessary, therefore, to insure the presence of ferric salts before attempting to precipitate chromium in this way. (See page 264.)

The Chromate Ion, $\mathrm{C\bar{r}O_4}$, and the Dichromate Ion, $\mathrm{C\bar{r}_2O_7}$.

Chromium trioxid, $\mathrm{CrO_3}$, is a red crystalline substance, readily soluble in water, forming orange-red solutions which have a decidedly acid reaction. On making neutral or alkaline, the color changes to yellow and there crystallizes out yellow salts of the type, $\mathrm{K_2CrO_4}$, which are known as chromates. Such yellow solutions contain the **chromate ion, $\mathrm{C\bar{r}O_4}$,** which is similar to the sulfate ion, $\mathrm{\bar{S}O_4}$. On acidifying a solution of a chromate, the color becomes orange-red and a red dichromate crystallizes, of which the potassium salt, $\mathrm{K_2Cr_2O_7}$, may be taken as typical. The orange-red solutions contain the **dichromate ion, $\mathrm{C\bar{r}_2O_7}$.**

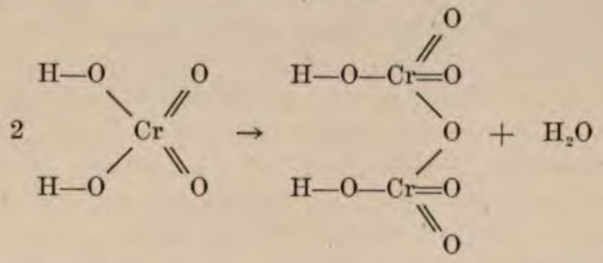
The chromate ion, $\mathrm{C\bar{r}O_4}$, is unstable in the presence of $\overset{+}{\mathrm{H}}$ ions while the $\mathrm{C\bar{r}_2O_7}$ ion is unstable in the presence of $\mathrm{\bar{O}H}$ ions. The change from the one into the other is expressed by the equations:

$$2\mathrm{C\bar{r}O_4} + 2\overset{+}{\mathrm{H}} \rightarrow \mathrm{C\bar{r}_2O_7} + \mathrm{H_2O}$$
$$\mathrm{C\bar{r}_2O_7} + 2\ \mathrm{\bar{O}H} \rightarrow 2\mathrm{C\bar{r}O_4} + \mathrm{H_2O}$$

For this reason, any attempt to obtain chromic acid, $\mathrm{H_2CrO_4}$, is unavailing and results only in dichromic acid, $\mathrm{H_2Cr_2O_7}$. Even this acid is known only in solution and every attempt to isolate it results in the anhydrid, CrO_3, according to the equation:

$$H_2Cr_2O_7 \rightarrow 2CrO_3 + H_2O$$

Dichromic acid may be derived theoretically by separating one molecule of H_2O from two molecules of H_2CrO_4:



Dichromic acid is, therefore, entirely analogous to other acids of the pyro- type and is to be considered as pyro-chromic acid. Since the difference between the acids is merely a question of dehydration, it would seem as though dichromic acid in dilute solution might become hydrated and changed into chromic acid, in a measure at least, by the mass action of the water. The same considerations would seem to indicate that a dichromate in dilute solutions might be changed into a chromate, partially at least. As a matter of fact this is so; for, if into solutions containing dichromate ions various kathions be introduced, metallic dichromates are seldom formed. In all dilute solutions chromates alone are formed, whether the original solution contained $\overset{=}{Cr_2}O_7$ or $\overset{=}{Cr}O_4$ ions. This phenomenon is largely explained by the fact that few dichromates are known except salts of the alkali and alkaline earth metals. Where both types are formed chromates are much less soluble, as a rule, than the corresponding dichromates and, therefore, are precipitated. The following equations illustrate this reaction:

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O \rightarrow$$
$$2\mathbf{PbCrO_4} + 2K(C_2H_3O_2) + 2H(C_2H_3O_2)$$

or writing an ionic equation:

$$2\overset{++}{Pb} + \overset{=}{Cr_2}O_7 + H_2O \rightarrow 2\mathbf{PbCrO_4} + 2\overset{+}{H}$$

Chromates show a close similarity to sulfates in many of their properties, and a comparison would seem to indicate that the hypothetical chromic acid is somewhat weaker than sulfuric acid. Chromates are readily soluble in the stronger acids, therefore, but do not dissolve in acetic acid. In high concentration, however, this last reagent is able to prevent the formation of a precipitate, although it is usually not strong enough to dissolve the salt when once brought down.

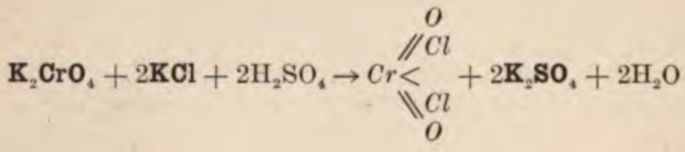
The alkali chromates are all very soluble, K_2CrO_4 being the most common salt. It dissolves in less than 2 parts of H_2O at ordinary temperatures and separates from solution without water of crystallization. The ammonium salt is similar to the potassium salt. The sodium salt, $Na_2CrO_4.10H_2O$, is very hydroscopic and melts in its own water of crystallization at temperatures but little above the ordinary. Because of the great solubility of these salts, they are ordinarily used as the reagents for introducing $\bar{C}rO_4$ ions into solutions of other salts.

Most chromates are soluble in water, the exceptions being the salts of silver, mercury in the lower condition, lead, copper, bismuth, tin and antimony in the lower condition, cobalt, nickel and barium.

All chromates are transposed by boiling with Na_2CO_3.

Of the **dichromates,** salts of the alkalies and alkaline earths, together with silver, mercury, lead and copper only, are well known. These are soluble or are decomposed by water.

Heated with concentrated H_2SO_4, chromates or dichromates, mixed with chlorids, give rise to a dark, reddish liquid, boiling at 117° and known as chloro-chromic anhydrid. Since the corresponding bromin and iodin compounds are not formed under the same conditions, this offers a means of differentiating between salts of the halogen elements (see page 299). The reaction by which chloro-chromic anhydrid is formed may be represented by the equation:

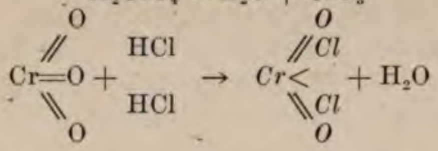


$$\mathbf{K_2CrO_4} + 2\mathbf{KCl} + 2H_2SO_4 \rightarrow \begin{array}{l} \quad O \\ \quad /\!/Cl \\ Cr< \\ \quad \backslash\!\backslash Cl \\ \quad O \end{array} + 2\mathbf{K_2SO_4} + 2H_2O$$

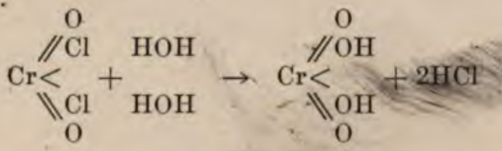
This equation represents, however, only the initial and final stages in the reaction and the true function of the concentrated H_2SO_4 is lost sight of. A better idea of the process may be obtained by a consideration of the following equations, which indicate the steps in the reaction:

$$\mathbf{K_2CrO_4} + H_2SO_4 \rightarrow \mathbf{K_2SO_4} + H_2CrO_4 \quad 2\mathbf{KCl} + H_2SO_4 \rightarrow \mathbf{K_2SO_4} + 2HCl$$

$$H_2CrO_4 \rightarrow H_2O + CrO_3$$



As will be noted, water is liberated during the process of formation of CrO_2Cl_2, but is prevented from decomposing the latter by the large excess of H_2SO_4 which is present. If, however, water is present in excess, it reacts with the chloro-chromic anhydrid exactly as it does with halogen compounds of non-metallic, *i. e.*, acid-forming elements generally. It is hydrolyzed with the formation of two acids, for *hexavalent* chromium is an acid-forming element.



The **barium ion, $\overset{++}{Ba}$,** added to dilute solutions containing chromates or dichromates, precipitates canary-colored barium chromate, $BaCrO_4$, insoluble in all alkalies. It is soluble in about 250,000 parts of water.

The **silver ion, $\overset{+}{Ag}$,** precipitates red silver chromate, Ag_2CrO_4, readily soluble in NH_4OH (see page 86). It dissolves in about 40,000 parts of H_2O.

The **lead ion, $\overset{++}{Pb}$,** precipitates deep yellow lead chromate, $PbCrO_4$, soluble in the strong alkalies (see page 145). It is very highly insoluble in pure water, requiring several hundred thousand parts of water for its solution. It is, however, much more soluble in traces of acids, bases and other salts.

The **mercurous ion, $(\overset{+}{Hg})_2$,** precipitates a brown basic chromate which, on boiling, changes to the fiery-red normal chromate, Hg_2CrO_4, insoluble in alkalies.

Group 7, First Type.

Fluorin 19; Chlorin 35.5; Bromin 80; Iodin 127.

The members of this most non-metallic and chemically-active group are known as halogens or "salt formers," sea-salt, NaCl, being a very common substance derived from one of the members of this group. The most characteristic valence is one; with the exception of fluorin, valences of five or seven, sometimes three, are shown by these elements in well-known compounds, however. The hydrids, of the type HCl, possess acid properties in a marked degree, hydrofluoric acid being considerably weaker than the others. The oxids of these elements are acid anhydrids but, with the exception of the iodin oxids, they generally possess little stability, being often explosive or entirely unknown. The acids formed by the union of these anhydrids with water are generally inclined to ready decomposition also. The stability as well as the strength of the acid increases as the valence of the halogen rises, however, and heptavalent compounds of the perchloric acid type, $HClO_4$, are very strong as well as very stable.

FLUORIN. F — 19.

Fluorin is a pale yellowish-green gas with a very pungent odor and toxic properties. It is the most reactive of all known substances. With the exception of oxygen and the inert argon group, it forms compounds with all the elements, many of which take fire spontaneously in it. Even at ordinary temperatures, in the presence of moisture, it unites with practically every substance, hence it does not exist free in nature, nor can it be preserved for a long time. For this reason, also, its isolation from its compounds was delayed for a long time. Water is decomposed with explosive violence even in the dark, hydrogen fluorid being formed, and oxygen, which is very rich in ozone, being set free. Chlorids, bromids and iodids are decomposed with the production of fluorids and the liberation of the halogen. (See similar action of chlorin, page 200.) Gold and platinum are not attacked by pure dry fluorin.

Fluorids may be considered as derived from hydrofluoric acid and their properties, as well as the reactions of the fluorid ion, $\bar{F}$, will be treated under this head.

Hydrofluoric Acid, HF.

Hydrogen fluorid is a colorless liquid (M. P.—92, B. P. 19.5°) with a strong pungent odor and very poisonous properties. It is very soluble in water, more than four hundred volumes of gas dissolving in one volume of water. A solution containing 35.5 per cent. of HF boils at 120° and is known as "concentrated hydrofluoric acid."

Hydrofluoric acid is a very corrosive liquid. It attacks all metals, except gold and platinum (lead only slightly); all oxids; many salts, and other substances of a different nature. Since glass is readily dissolved by hydrofluoric acid, the latter must be preserved in containers made of paraffine, rubber, or a few other materials which are not attacked by it.

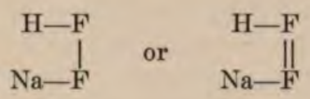
It causes very painful, poisonous, slow-healing burns when in contact with the flesh.

The **etching of glass** is one of the most important reactions of hydrofluoric acid. Glass is essentially a mixture of several salts of the various polysilicic acids. The composition of soda glass may be represented by the formula, $Na_2Si_3O_7.CaSi_3O_7$, and the action of hydrofluoric acid by the equation:

$$\mathbf{Na_2Si_3O_7.CaSi_3O_7} + 28HF \rightarrow 2NaF + \mathbf{CaF_2} + \mathit{6SiF_4} + 14H_2O$$

A very delicate test for hydrofluoric acid depends upon this reaction. (See page 278.)

Hydrofluoric acid is usually considered as a monobasic acid and, as such, ought not to form true acid salts (see page 21). Salts of this character are well-known, however. An investigation of the molecular weight of hydrogen fluorid indicates that, at 100° and above, the molecule is HF but that, at ordinary temperatures, it doubles up and has the formula $(HF)_2$. Acid salts such as $HNaF_2$ and HKF_2 are readily explained by some such formulae as the following:



$$\begin{array}{r} H\text{—}F \\ | \\ Na\text{—}F \end{array} \quad \text{or} \quad \begin{array}{r} H\text{—}F \\ \| \\ Na\text{—}F \end{array}$$

Hydrogen fluorid acts as a comparatively weak acid, dissociating to an extent much less than the corresponding acids formed by the other halogen elements. In solution, fluorids are hydrolyzed to some extent and glass containers are etched by the liberated hydrofluoric acid on long standing.

On ignition, fluorids fuse unchanged, some of them being volatile at temperatures easily attainable.

Heated with concentrated H_2SO_4, all fluorids are changed to sulfates and hydrofluoric acid volatilized.

Salts of hydrofluoric acid differ in their solubility reactions very much from the corresponding chlorids, bromids and iodids. Most fluorids are soluble; the copper, lead, zinc and ferric salts dissolve sparingly and the salts of the alkaline earths are quite insoluble.

All fluorids formed by precipitation are readily transposed by boiling with Na_2CO_3.

The simple **fluorid ion** is $\bar{\mathbf{F}}$. Several complex ions containing fluorin are recognized. Of these the silicofluorid ion, $\overline{Si}F_6$, is the best known. (See page 136.)

The **barium ion, $\overset{++}{\mathrm{Ba}}$,** added to a solution containing the fluorid ion, causes a voluminous white precipitate, BaF_2, soluble in large amounts of the stronger acids and in ammonium chlorid.

The **calcium ion, $\overset{++}{\mathrm{Ca}}$,** precipitates white CaF_2, which is somewhat less soluble than the corresponding barium salt. The naturally-occurring compound, fluorspar, is however, one of the most insoluble substances known. In order to get it completely into solution, it is usually necessary to fuse it with Na_2CO_3, to which some silica or a silicate has been added. Silica aids in the decomposition of the calcium fluorid by the formation of calcium silicofluorid as an intermediate product which is later decomposed by the carbonate.

The **silver ion, $\overset{+}{\mathrm{Ag}}$,** causes no precipitation, for silver fluorid is readily soluble.

CHLORIN. Cl — 35.5.

Chlorin is a yellowish-green gas with a suffocating and nauseous odor. It is somewhat soluble in water, two volumes of gas forming a solution which is known as "chlorin water," from which all chlorin may be removed by boiling. At zero, chlorin unites with water to form a crystalline hydrate of the composition $Cl_2.8H_2O$, which at higher temperatures breaks down again into its components. The element is also soluble in carbon disulfid, chloroform and ether, giving colorless solutions.

Chlorin is a typical non-metallic element and is surpassed in chemical activity by fluorin only. It combines readily with all metals and with many of the non-metallic elements, often causing them to burst into spontaneous combustion. It unites with hydrogen, to form hydrogen chlorid, so vigorously that it will abstract this element from many of its compounds. Even the very stable body, water, is slowly decomposed with the liberation of oxygen. Bromids and iodids in solution are changed to chlorids and the halogen is set free.

Chlorin passes with the greatest readiness into the ionic condition, forming the simple ion, $\bar{\mathrm{Cl}}$. On the basis of this property, the decomposition of water and of bromids and iodids in solution is to be explained, for chlorin shows a greater tendency to assume the electric charge than oxygen, bromin or iodin do to hold it (see page 327). Hence, the charge passes from these elements, which are thus set free, and is taken up by the chlorin, which becomes the chlorin ion, as the equations show:

$$\bar{\mathrm{O}} + 2\mathrm{Cl} \rightarrow 2\bar{\mathrm{Cl}} + O \quad \text{or} \quad 2\,\bar{\mathrm{O}}\mathrm{H} + 2\mathrm{Cl} \rightarrow 2\bar{\mathrm{Cl}} + \mathrm{H_2O} + O$$

$$\bar{\mathrm{Br}} + \mathrm{Cl} \rightarrow \bar{\mathrm{Cl}} + \mathrm{Br} \qquad \bar{\mathrm{I}} + \mathrm{Cl} \rightarrow \bar{\mathrm{Cl}} + \mathbf{I}$$

Chlorin is one of the strongest oxidizing agents, carrying substances generally to the highest degree of oxidation capable under the conditions of the experiment. Its action on water establishes its oxygen equivalent, two atoms of chlorin being equivalent to one atom of oxygen, as the equation shows:

$$2Cl + H_2O \rightarrow 2HCl + O$$

Chlorin possesses very strong bleaching properties, litmus, turmeric, indigo and other organic dye-stuffs being immediately destroyed by the moist gas or its solution in water. The dry gas is without appreciable effect, however, and the bleaching action of moist chlorin is apparently to be attributed to nascent oxygen set free by the decomposition of the water present.

Chlorin acts on cold dilute solutions of the strong bases to form chlorids and hypochlorites in equal proportions, as the equation indicates:

$$2Cl + 2KOH \rightarrow KCl + KOCl + H_2O$$

If the solution be heated or is concentrated, chlorates (along with chlorids) are formed instead of hypochlorites, owing to the decomposition of the latter (see page 204). If alkaline carbonates are substituted for the hydroxids in the above reactions, the same products are formed and carbon dioxid is driven out.

With oxygen, chlorin does not unite directly but, by the decomposition of certain oxygen acids of chlorin, three oxids can be obtained having the composition indicated by the formulae—Cl_2O, ClO_2 and Cl_2O_7. These bodies will be considered under the respective acids from which they are derived.

United with oxygen, chlorin forms several anions, of which the most important, the hypochlorite ion, $O\bar{C}l$, the chlorate ion, $Cl\bar{O}_3$, and the perchlorate ion, $Cl\bar{O}_4$, will be treated under the respective acids from which they are derived. Inasmuch as the compounds formed by the simple chlorin ion, $\bar{C}l$, may be considered as salts of hydrochloric acid, the reactions of this ion and the properties of the salts will be considered under this head.

Free chlorin is usually detected by its odor, bleaching properties and action on bromids and iodids. These reactions serve to distinguish it from all reagents except hypochlorous acid, which has bleaching properties, the same action on bromids and iodids and an odor closely resembling chlorin. Metallic mercury offers a satisfactory means of differentiation, for chlorin forms white mercurous chlorid, $(HgCl)_2$, insoluble in

HCl, whereas hypochlorous acid forms brown mercuric oxychlorid, Hg_2Cl_2O, which is readily soluble in HCl. Hydrochloric acid is without effect on mercury; therefore, the solution to be tested is slightly acidified with HCl and shaken with mercury until it no longer turns a drop of starch-iodid solution blue. A brown precipitate indicates hypochlorous acid, a white precipitate free chlorin. In case the indication is doubtful, the solution may be decanted and the precipitate treated with HCl when the brown oxychlorid will dissolve, leaving behind white mercurous chlorid if free chlorin was present. Hydrogen sulfid passed into the HCl extract will produce a black precipitate of HgS if hypochlorous acid was present.

Hydrochloric Acid, HCl.

Hydrogen chlorid is a colorless gas with a sour taste and sharp pungent odor. It fumes in the air and dissolves abundantly in water, 450 volumes of gas requiring only one volume of water for solution. Its aqueous solution reacts strongly acid to litmus and is known as hydrochloric acid. "**Concentrated hydrochloric acid**" is a solution which is about saturated at ordinary temperatures and contains 38–39 per cent. HCl and 61–62 per cent. H_2O. A solution containing 20 per cent. HCl boils constant at 110°, hence hydrogen chlorid cannot be removed completely from solution by boiling; for, on heating, any solution loses mainly either water or hydrogen chlorid until the composition of the liquid in the vessel becomes 20 per cent. HCl and 80 per cent. H_2O. This solution then distills over without change. (See similar action of HNO_3, page 150.)

Hydrogen chlorid is a very stable compound and in dilute solutions does not yield readily to oxidizing or reducing agents. Strong oxidizing agents such as $HMnO_4$, $HClO_3$, HClO, HNO_3, HNO_2, $H_2Cr_2O_7$ and H_2O_2, however, oxidize it to free chlorin and water, especially in concentrated solutions, although in dilute solution the action is often inappreciable. When a dry chlorid is mixed with powdered $K_2Cr_2O_7$ and heated with concentrated H_2SO_4, the chlorin first liberated by the reaction unites with chromium trioxid, another reaction product, to form CrO_2Cl_2, a reddish-brown gas under the conditions of this experiment. This reaction is often used as a test for HCl. (See pages 196 and 299.)

Hydrochloric acid acts as one of the very strongest monobasic acids, in solutions of ordinary dilution being practically completely ionized.

Salts of hydrochloric acid *are soluble,* as a rule. The chlorids of silver and of mercury, copper, gold and platinum in the lower form are highly insoluble, however. Lead chlorid may be precipitated from cold solutions containing above one per cent. of lead but it is readily soluble in hot water. The commonly-occurring oxychlorids of bismuth and antimony are also insoluble.

On ignition in the air, most metallic chlorids fuse unchanged and volatilize at a higher temperature. Mercuric chlorid melts at 265° and boils at 307°, lower than other metallic chlorids. When a metal forms more than one chlorid, the higher form generally breaks down into the lower. The chlorids of gold and platinum lose all their halogen and decompose into the metals. Chlorids of trivalent metals are generally changed to the corresponding oxids with the liberation of the halogen.

Heated with concentrated H_2SO_4, all chlorids are changed to sulfates and HCl is liberated. This reaction is not to be explained by the assumption that H_2SO_4 is stronger than HCl (for the converse is true), but it is entirely due to the fact that HCl is much more volatile than H_2SO_4 and is therefore driven off. (See page 27.)

All chlorids are transposed by boiling with Na_2CO_3, except silver chlorid, which requires fusion with the dry reagent. Silver carbonate, the first reaction product, breaks down into the metal, carbon dioxid and oxygen.

The **barium ion, $\overset{++}{Ba}$,** added to a solution containing the **chlorid ion, $\overset{-}{Cl}$,** causes no precipitate, for $BaCl_2$ is readily soluble.

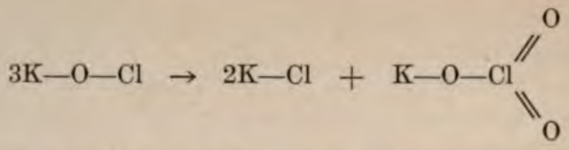
The **silver ion, $\overset{+}{Ag}$,** precipitates curdy white AgCl, darkening in the sun-light. (See page 86.)

The **lead ion, $\overset{++}{Pb}$,** precipitates white $PbCl_2$ from cold solutions which are not too dilute. (See page 145.)

The **mercurous ion, $(\overset{+}{Hg})_2$,** precipitates white $(HgCl)_2$. (See page 111.)

Hypochlorous Acid, HClO.

Salts of hypochlorous acid may be produced by the action of chlorin on alkalies or alkaline carbonates, as has been previously stated. If nitric or sulfuric acid be added to such a solution, hypochlorous acid is liberated but, on every attempt to isolate it, its decomposition products only, chiefly chlorin, oxygen and hydrochloric acid, are obtained. This is due, partially to the formation of the anhydrid, Cl_2O, an exceedingly unstable substance which decomposes immediately into its elements, and partially to a general reaction of all hypochlorites. When in concentrated solution or when warmed, they undergo a reaction, forming chlorids and chlorates in equal proportions, as the equation shows:



$$3\mathrm{K{-}O{-}Cl} \rightarrow 2\mathrm{K{-}Cl} + \mathrm{K{-}O{-}Cl}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash\!\!\backslash\mathrm{O}}$$

Hypochlorous acid acts as a monobasic acid but it is so weak that the carbon dioxid of the atmosphere liberates it from its salts. Hence it is that hypochlorites, exposed to the air, are soon decomposed entirely. Further indication of the weakness of hypochlorous acid is furnished by the fact that solutions of the salts formed by the alkali metals react strongly basic because of hydrolysis.

All hypochlorites possess strong bleaching properties. This is explained by the fact that they are vigorous oxidizing agents. In the presence of reducing matter, each molecule of hypochlorite gives up one atom of oxygen and becomes a chlorid. Bleaching takes place in alkaline as well as in neutral and acid solutions, a reaction serving to differentiate hypochlorites from other compounds of chlorin. The bleaching action is most rapid in acid solution because of the greater instability of the free acid than of the salts. "Chloride of lime," the great commercial bleaching salt, is a mixture of calcium chlorid with the hypochlorite, made by passing chlorin over slacked lime.

All hypochlorites are accompanied by chlorids because of the method of their formation, hence when any ordinary acid is added to a solution of a hypochlorite, hydrochloric acid, as well as hypochlorous acid, is liberated. These reagents interact; the hydrochloric acid is oxidized and chlorin becomes the chief decomposition product under these conditions.

$$HCl + HOCl \rightarrow H_2O + Cl_2$$

Inasmuch as chlorin water cannot be preserved for any considerable time, an acidified solution of a hypochlorite is often used instead of the other more dilute reagent.

All hypochlorites are soluble and may be transposed by boiling with Na_2CO_3. The ammonium salt is unknown, for, on bringing together ammonia and hypochlorous acid, as fast as the ammonium hypochlorite is formed, it interacts with the remaining ammonia and is decomposed, according to the equation:

$$3NH_4ClO + 2NH_3 \rightarrow 3NH_4Cl + 3H_2O + N_2$$

The **barium ion, $\overset{++}{\mathrm{Ba}}$,** added to a solution containing the **hypochlorite ion, $\overset{-}{\mathrm{ClO}}$,** causes no precipitation.

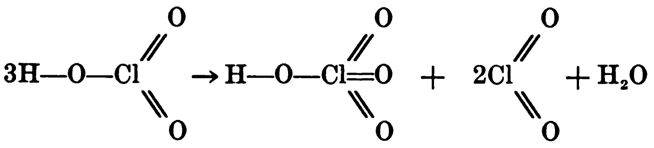
The **silver ion, $\overset{+}{Ag}$,** precipitates white AgCl, owing to the almost immediate decomposition of the soluble silver hypochlorite according to the regular equation:

$$3AgClO \rightarrow AgClO_3 + 2\mathbf{AgCl}$$

One-third of the silver remains in solution as the chlorate, however, as the equation shows.

Chloric Acid, $HClO_3$.

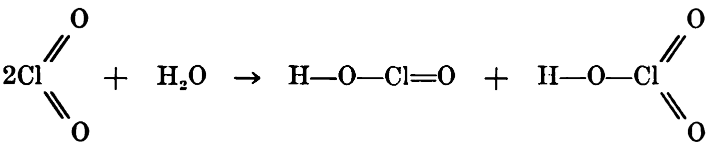
Although **chloric acid** is considerably more stable than hypochlorous acid, like the latter it is known only in solution and attempts to isolate it give only decomposition products:



$$3H{-}O{-}\overset{O}{\underset{O}{Cl}} \rightarrow H{-}O{-}\overset{O}{\underset{O}{Cl}}{=}O + 2\overset{O}{\underset{O}{Cl}} + H_2O$$

On adding an acid to a chlorate, therefore, ClO_2 is an important decomposition product.

Chlorin dioxid is a heavy yellowish-brown gas with stifling odor. It often decomposes spontaneously with explosive violence into the elements. Its solution in water is more stable and, after a time, takes an acid reaction. After neutralizing with an alkali, evaporation of the solution leaves a residue consisting of a chlorate and a chlorite. The corresponding chlorous acid, $HClO_2$, is unknown except in dilute solution, and its salts are of little importance. (See also page 148.)



$$2\overset{O}{\underset{O}{Cl}} + H_2O \rightarrow H{-}O{-}Cl{=}O + H{-}O{-}\overset{O}{\underset{O}{Cl}}$$

Chlorin dioxid, being so unstable and breaking down into nascent oxygen and chlorin, is one of the most vigorous oxidizing agents known. For this reason, a solution of chloric acid has strong oxidizing and bleaching properties but, unlike hypochlorites, chlorates bleach only in acid and not in neutral or alkaline solutions; for chlorates, in solution, are stable and only chloric acid decomposes in the manner stated.

When a chlorate is acidified with HCl, much of the latter is oxidized by the free chloric acid, which is liberated, or by its decomposition product, ClO_2. Free chlorin is liberated in abundance, therefore.

$$KClO_3 + 6HCl \rightarrow KCl + 3H_2O + \mathit{6Cl}$$

If HNO_3 or H_2SO_4 be substituted for HCl, chlorin dioxid is the main product and an explosion results, especially if the acid be concentrated and the mixture heated. Hence nothing larger than a very minute crystal of a chlorate should ever be heated with concentrated H_2SO_4.

The **salts of chloric acid** are the salts of a very strong acid. They are considerably more stable than hypochlorites and are not decomposed by exposure to the atmosphere or on gentle warming. On heating, however, a general reaction of all chlorates takes place, resulting in the formation of perchlorates and chlorids and the liberation of one-third of their oxygen content.

$$\mathbf{2KClO_3 \rightarrow KClO_4 + KCl} + O_2$$

Since perchlorates, on further heating, break down into chlorids according to the reaction given on page 207, oxygen in large proportion is liberated in this reaction. The presence of small amounts of PbO_2, MnO_2, Fe_2O_3, CuO or certain other finely divided substances causes the gas to be liberated more rapidly and at a lower temperature.

All chlorates are good oxidizing agents because of this decomposition and they are used especially in high-temperature reactions performed in the "dry way." Matches, "fire-works" and certain explosives consist of mixtures of chlorates with some combustible substance. In the presence of reducing agents, the formation of perchlorates does not take place, hence each molecule of chlorate liberates three atoms of oxygen.

Under the influence of strong reducing agents, chlorates are reduced to chlorids either in acid or alkaline solution, and in this way chlorates may be differentiated from the more stable perchlorates which are not broken down by the ordinary reducing agents.

Chloric acid acts as a very strong monobasic acid and, like nitric acid, which it resembles in many of its properties, it colors a brucin solution red.

All chlorates are soluble, the potassium salt, requiring 21 parts of water for its solution, dissolving with the least readiness.

All chlorates are transposed by boiling with Na_2CO_3.

The **barium ion,** $\overset{++}{\mathbf{Ba}}$, added to a solution containing the **chlorate ion,** $\mathbf{ClO_4}$, gives no precipitate, for $BaClO_3$ is readily soluble.

The **silver ion,** $\overset{+}{\mathbf{Ag}}$, causes no precipitation, for $AgClO_3$ is soluble.

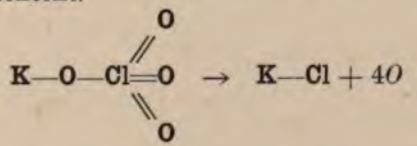
Perchloric Acid, $HClO_4$.

Perchloric acid is a colorless, fuming, oily liquid, by far the most stable of any of the oxygen acids of chlorin; yet it is little known in the pure state because of its tendency to decompose explosively. With water, it unites to form a crystalline hydrate, $HClO_4.H_2O$ which decomposes at 110°. A second hydrate, $HClO_4.2H_2O$, distills undecomposed at 203° and, since it is perfectly stable, this hydrate is the form in which perchloric acid is best known.

Perchloric acid is one of the very strongest acids and in aqueous solution is almost completely dissociated into its ions. In solution, perchlorates show but little tendency to break down, even when subjected to a great variety of conditions. Although **perchlorates** contain a greater percentage of oxygen than the salts of any other chlorin acids, they are not by any means good oxidizing agents; for, because of their stability, they do not readily give up any of their oxygen. Hence, perchlorates do not possess any bleaching properties even in boiling acid solutions and ordinary reducing agents, such as zinc dust, Devarda's alloy, sulfurous acid and stannous or ferrous chlorids are without effect. Since reactions in solution are mainly the reactions of ions, the stability of perchlorates in aqueous solution is to be attributed to the stability of the perchlorate ion.

The undissociated acid and salts are not by any means as stable, hence the danger of explosion in attempting to handle pure perchloric acid. This may be explained, partially, by the fact that perchloric anhydrid, Cl_2O_7, a colorless oily liquid—B. P. 82°—is liable to spontaneous explosion.

Ignition of perchlorates decomposes them into chlorids and liberates their full oxygen content.



$$\mathrm{K{-}O{-}\overset{\overset{O}{/\!/}}{\underset{\underset{O}{\backslash\backslash}}{Cl}}{=}O \rightarrow K{-}Cl + 4\mathit{O}}$$

The resistance to reducing agents offered by perchlorates in solution and their ready decomposition when the dry substance is heated, serves to distinguish perchlorates from salts of all other chlorin acids. For, on treating a solution with sulfurous acid or some similar body, hypochlorites and chlorates are reduced to chlorids and may be removed from solution by precipitation with silver nitrate. If the filtered solution be evaporated, the residue ignited and the aqueous extract again treated with $AgNO_3$, any further precipitation will be due to the decomposition of perchlorates. (See page 306.)

All perchlorates are soluble, the potassium salt, requiring about 100 parts of water for its solution, being the most insoluble.

All perchlorates are transposed by boiling with Na_2CO_3.

The **barium ion, $\overset{++}{\mathrm{Ba}}$,** added to a solution containing the **perchlorate ion, $\overset{-}{\mathrm{ClO_4}}$** causes no precipitation.

The **silver ion, $\overset{+}{\mathrm{Ag}}$,** gives no precipitate.

BROMIN. Br — 80.

Bromin is a heavy, dark brownish-red liquid, sharing with mercury the distinction of being the only elements existing normally in the liquid state. It passes readily into the gaseous phase, however, when exposed to the air at ordinary temperatures, forming a heavy red vapor which attacks the mucous membranes of the nose, eyes and throat, causing serious discomfort. It is soluble in about 30 parts of water, forming a solution known as "bromin water," from which all the halogen may be removed by boiling. The presence of a soluble bromid in solution renders the bromin somewhat more soluble. The increase in solubility is not equal to that caused by the addition of iodids to an aqueous solution of iodin but it is doubtless to be explained on the same basis (see page 210). Bromin is so much more soluble in carbon disulfid, chloroform and ether than it is in water that it may be removed from its aqueous solution by shaking with any of these liquids. These solvents form solutions the color of which varies from orange-yellow to brownish-red depending on the concentration of the bromin.

Bromin very closely resembles chlorin in chemical properties but its action is less energetic. All of its reactions are so closely analogous to those of chlorin that a detailed description will be unnecessary. It unites with most of the elements, forming bromids, of which hydrogen bromid is the most important. It abstracts hydrogen and liberates oxygen only very slowly from water, but it attacks solutions of iodids, setting free this halogen and forming bromids. The reactions are explained by the fact that bromin passes more readily into the ionic condition than iodin or oxygen do. (See page 327.)

Bromin acts as a very strong oxidizing agent and possesses bleaching properties similar to those of chlorin, the oxygen equivalent of both halogens being the same. On alkalies, the action is analogous and hypobromites and bromates are formed under identical conditions. Inasmuch as these compounds are of far less importance than the corresponding compounds of chlorin, since the properties of the two are so very similar, hypobromous and bromic acids will not be considered in detail. No acids or salts of bromin analogous to chlorous and perchloric acids are known, nor have any oxids of bromin been discovered.

Free bromin is usually detected by its odor, color, bleaching properties and action on iodids.

Hydrobomic Acid, HBr.

Hydrogen bromid is a colorless gas with sharp odor and acid taste, closely allied to hydrogen chlorid in all its properties. It fumes strongly in the air and dissolves abundantly in water, forming a solution known as hydrobromic acid. A saturated solution consists of about 80 per cent. HBr and 20 per cent. H_2O.

Hydrogen bromid is much less stable than hydrogen chlorid, hence it yields far more readily to reagents generally. Oxidizing agents convert it into free bromin and water, especially in concentrated solutions. Atmospheric oxygen is sufficient to oxidize it slowly, hence solution of hydrobromic acid soon turn dark because of the liberated bromin. Because of the presence of the free halogen, the corrosive action of hydrobromic acid is very great and it will dissolve several metals not appreciably acted upon by hydrochloric acid.

If free chlorin be used as an oxidizing agent, as is frequently the case in testing for bromids, hydrogen chlorid is formed in place of hydrogen oxid, *i. e.*, water. If a great excess of chlorin be present, it may unite with the liberated bromin to form bromin chlorid, BrCl, which, although decomposed by water, may exist in carbon disulfid or chloroform, giving solutions which lack the red color due to bromin and are nearly colorless.

Hydrobromic acid is quite as completely dissociated in aqueous solution as is hydrochloric acid. It acts as a monobasic acid and forms salts, the solubility of which corresponds almost exactly with that of the chlorids.

Ignition of bromids produces the same effect as with chlorids. Usually the salt fuses unchanged and volatilizes as the temperature is raised.

Heated with concentrated H_2SO_4, all bromids are converted into sulfates and hydrobromic acid is liberated. Hot concentrated H_2SO_4 possesses oxidizing properties (see page 187) sufficient to decompose some of the HBr set free. Hence free bromin can always be detected, together with the reduction products of H_2SO_4, generally SO_2.

All bromids are transposed by boiling with Na_2CO_3 with the exception of silver bromid which, like the other halogen compounds of silver, requires fusion with the dry reagent. (See page 203.)

The **barium ion, $\overset{++}{Ba}$,** added to a solution containing the **bromid ion, $\overset{-}{Br}$,** gives no precipitate, for $BaBr_2$ is soluble.

The **silver ion, $\overset{+}{Ag}$,** precipitates white AgBr. (See page 87.)

IODIN. I — 127.

Iodin is a dark gray, almost black, crystalline solid, possessing a metallic lustre. It fuses at 114° and boils at 184°, forming a deep violet vapor. If the temperature be maintained just below its melting-point, however, the solid may be readily sublimed. It is quite insoluble in water, one part of iodin requiring about 5000 parts of water for solution. The presence of a soluble iodid greatly increases its solubility, this action being due to the formation of a periodid which gives rise to the ion $\overset{-}{I_3}$.

$$KI + 2I \rightarrow KI_3 \rightarrow \overset{+}{K} + \overset{-}{I_3}$$

This ion is stable only in the presence of free iodin and as fast as the free halogen is removed in any reaction, the periodid decomposes into the simple iodid, so that all the free iodin originally put into solution is available.

Iodin dissolves very readily in carbon disulfid, chloroform, ether and alcohol and may be removed from aqueous solutions by shaking with any of these solvents, alcohol being excepted because it is miscible with water. Carbon disulfid and chloroform give rise to purple solutions, while ether and alcohol are colored brown.

Iodin produces a brown stain when brought into contact with the person. The application of ammonia to a fresh stain will remove it.

Iodin closely resembles bromin and chlorin in chemical properties, but its action is far less energetic and temperatures higher than the ordinary are usually required to make it unite directly with other elements. It forms an unstable compound with hydrogen, hence it does not appreciably decompose water as the other halogens do.

Iodin acts as a very weak oxidizing agent. Its oxygen equivalent is exactly that of chlorin and bromin, but its action is by no means as vigorous. Many substances which are oxidized by the latter elements do not interact with iodin and the oxidization products formed by iodin, when it does react, are frequently not so highly oxidized as are the reaction products when chlorin and bromin are used. (See page 189.)

With **starch** in aqueous solution, iodin produces a deep blue color which is due to a body formed by the addition of the iodin to the starch. By adding alcohol or by boiling a solution containing the starch-iodid compound, it is decomposed and the blue color vanishes, to reappear on dilution or on cooling, provided the boiling has not been continued too long.

Free iodin is usually detected by the starch-iodid reaction, the color of its vapor, or of its solutions in carbon disulfid or chloroform.

Iodin acts on alkalies in a manner exactly analogous to chlorin and bromin, forming hypoiodites and iodates. **Hypoidites,** however, are more unstable than the corresponding salts of the other halogens and they have only a temporary existence even in solution.

Iodic acid, HIO_3, is a white crystalline solid, very soluble in water. At 170° it loses water, forming the colorless crystalline anhydrid, I_2O_5, which decomposes into its elements at 300°. Iodic acid acts as a very strong monobasic acid, forming salts which are not as soluble as the corresponding chlorates. Few iodates are highly insoluble, however, the silver salt, requiring about 27,000 parts of water being the least soluble.

Periodates cannot be formed by heating iodates, analogous to the method for the production of perchlorates; for, on ignition, iodates break down into iodids or oxids. Periodic acid may be formed by the action, in alkaline solution or in the "dry way," of very strong oxidizing agents on iodin. In its general reactions it resembles iodic acid.

Hydriodic Acid, HI.

Hydrogen iodid, like the hydrogen compounds of other halogens, is a colorless gas with sharp, pungent odor and acid taste. It is abundantly soluble in water, the solution being known as **hydriodic acid.**

Hydrogen iodid is far less stable than any other halogen compound of hydrogen. The dry gas decomposes very largely into hydrogen and iodin, and aqueous solutions turn dark after a very short time because of the separation of iodin. This spontaneous decomposition into its elements makes hydriodic acid a very strong reducing agent, even in dilute solution,—a property which hydrochloric and hydrobromic acids show only in concentrated solutions. Hence, in the presence of substances which can be made to part with a portion of their oxygen or other equivalent element, hydriodic acid reacts vigorously.

Ordinary oxidizing agents convert hydriodic acid into free iodin and water, but vigorous reagents, such as permanganate and chlorin in excess, oxidize the liberated iodin to iodic acid, HIO_3. In carbon disulfid or chloroform colorless ICl may be formed. (See also page 209.)

An idea of the comparative stability of the hydrogen compounds of the halogens may be gained by a consideration of the following facts.

Nitrous acid liberates iodin from dilute solutions of hydriodic acid, but does not oxidize hydrochloric or hydrobromic acids except in concentrated solutions. Hydrofluoric acid is not oxidized under any conditions by nitrous acid or any other oxidizing agent. Dichromic acid in dilute solutions sets free iodin; bromin is liberated if the solution be somewhat more concentrated, but hydrochloric acid is oxidized only in concentrated solutions.

Hydriodic acid is very completely dissociated in aqueous solution and, though very unstable, is quite as strong as the other more stable halogen acids. It is monobasic and forms salts, the solubility of which agrees very closely with that of the chlorids, with the exception that mercuric iodid is quite insoluble.

Ignition of iodids indicates the unstable character of the acid from which they are derived; for, when heated in the atmosphere, they are converted into the oxid of the metal with the liberation of iodin. The salts of the alkali metals are most stable and may be fused without appreciable decomposition.

Heated with concentrated H_2SO_4, all iodids are converted into sulfates, and iodin and water are liberated; for the hydriodic acid, at first set free, is oxidized by the hot H_2SO_4. As reduction products of the latter, sulfur dioxid, sulfur and hydrogen sulfid may appear.

All iodids are transposed by boiling with Na_2CO_3, except silver iodid, which may be decomposed by fusion with the dry reagent. (See page 203.)

The **barium ion, $\overset{++}{Ba}$,** added to a solution containing the **iodid ion, $\overset{-}{I}$,** causes no precipitation, for BaI_2 is soluble.

The **siver ion, $\overset{+}{Ag}$,** precipitates yellow AgI. (See page 87.)

The **lead ion, $\overset{++}{Pb}$,** precipitates golden-yellow PbI_2. (See page 145.)

The **mercuric ion, $\overset{++}{Hg}$,** precipitates vermilion HgI_2. (See page 109.)

The **mercurous ion, $(\overset{+}{Hg})_2$,** precipitates olive $(HgI)_2$. (See page 111.)

Group 7, Second Type.

Manganese 55.

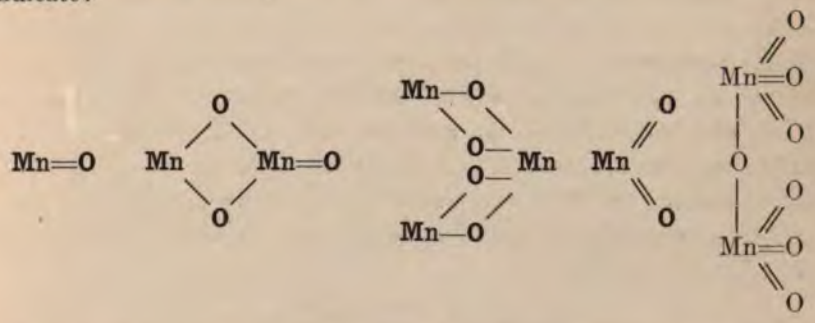
Manganese is the only known element of this type. It stands in about the same relation to the halogen group that chromium does to the sulfur group. In the free state, manganese is a typical metal and, while forming compounds which show a close similarity in chemical formula, the properties of many of its compounds are quite different from the corresponding compounds of the halogen elements. In the divalent and trivalent conditions, manganese acts as a weak base-forming element; tetravalent manganese is intermediate in character, like tetravalent lead or tin, while hexavalent and heptavalent manganese possess strong acid-forming properties. It is only in this last stage of oxidation that manganese shows similarity to the halogen group.

MANGANESE. Mn — 55.

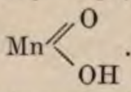
Manganese is a brittle, grayish-white metal. Although it is an almost constant companion of iron in natural compounds, the pure metal is exceedingly uncommon. It is readily attacked by the constituents of the atmosphere, forming oxids or "rusts."

Manganese dissolves readily, even in acetic acid, forming salts in which the metal is bivalent and acts as a base-forming element. During the passage into the ionic condition, a large amount of energy is liberated. This causes the salts to be exceedingly difficult to reduce to the metal. On the other hand, the whole tendency of the element is to pass into a state of higher oxidation, becoming successively tri-, tetra-, hexa-, and finally hepta-valent. As the valence increases, there is a gradual disappearance of the basic properties which characterize the bivalent condition and a corresponding increase in acidic properties until the strongly acid heptavalent condition is reached. (See page 45.)

Five **oxids of manganese** are known, as the following formulae indicate:



Divalent manganese oxid, MnO, is the only oxid readily and completely soluble in dilute acids. There is formed in this way a whole series of salts in which the metal is bivalent and acts as a base-forming element, about as strong as ferrous iron or zinc. Manganese salts are pale pink when containing water of crystallization. In solution the color is not of sufficient intensity to be noticeable. Anhydrous salts are generally colorless. Hydrolysis does not take place in cold solutions to an extent sufficient to cause precipitation of the hydroxid when the free acid in solution is neutralized by the addition of $BaCO_3$ or similar compounds.

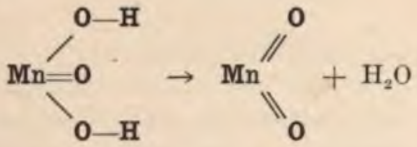
Trivalent manganese is but little known and is unimportant. Only a few stable compounds are definitely known—the sulfate, $Mn_2(SO_4)_3$, and the "alum," $Mn_2(SO_4)_3.K_2SO_4.24H_2O$, or better, $KMn(SO_4)_2.12H_2O$, besides, possibly, the hydroxid,  $Mn\begin{smallmatrix}/\!\!/O\\ \diagdown OH\end{smallmatrix}$. Other salts are known only in concentrated solutions of their respective acids and are decomposed by heat and dilution. They are of a dark brown color (see page 277). A consideration of all the known facts indicates that trivalent manganese is a weaker base-forming element than manganese in the divalent condition.

Tetravalent manganese is better known and acts as a very weak base-forming as well as weak acid-forming element. This is suggested by the fact that the black dioxid, MnO_2, is not acted upon by dilute acids in the cold. Fairly concentrated acid is necessary to dissolve it. When so treated, there is evidence of the existence of salts, such as $MnCl_4$, in the dark-colored solution, but they are less stable than the trivalent salts and, on heating or on dilution, they decompose according to the typical reaction:

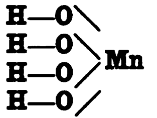
$$MnCl_4 \rightarrow MnCl_2 + \mathit{Cl}_2$$

No salts are known out of solution.

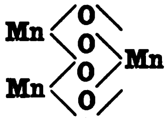
The partially-dehydrated hydroxid, $MnO(OH)_2$, is known as (meta) manganous acid, for it turns litmus red slowly and acts as a weak acid. It is but little soluble in alkalies because the alkali manganites are but little soluble and, furthermore, are almost completely hydrolyzed. In acids it dissolves, forming the unstable salts already mentioned, thus showing that its nature has been made basic by the presence of the stronger acids. If H_2MnO_3 be an acid like H_2CO_3 or H_2SnO_3, then MnO_2 is an acid anhydrid, as the equation shows, and its insolubility in dilute acids is thus explained.



When Mn_3O_4, like Pb_3O_4 (see page 143), is treated with dilute acids two-thirds of the manganese is dissolved while one-third is left behind as insoluble MnO_2. It is therefore to be regarded as the manganous salt of ortho-manganous acid (not definitely known), as is indicated by the formulae:

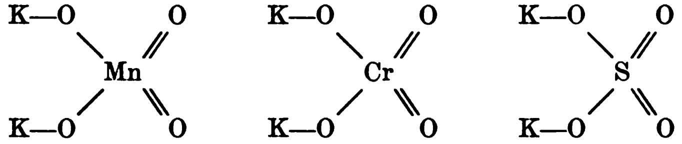


Ortho-manganous acid.



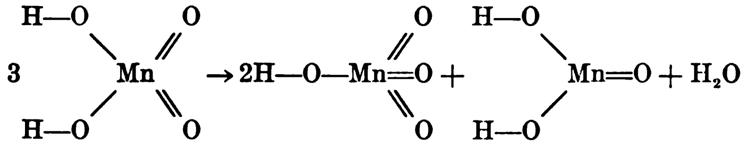
Manganous ortho-manganite.

Hexavalent manganese acts as an acid-forming element entirely and possesses no base-forming properties. All manganese compounds, whether higher or lower oxidized, come into this condition on heating with alkalies, forming intensely green salts of manganic acid which are analogous to chromates and sulfates as the formulae indicate:



The properties of these salts would indicate that H_2MnO_4 is a much stronger acid than H_2MnO_3, but not quite so strong as chromic acid.

The acid itself is entirely unknown for, as soon as it is set free from one of its salts, it decomposes into a higher and a lower oxidized product, as the equation shows:



The solution of a manganate is green in color. It contains the ion, $M\overset{=}{n}O_4$, which is stable only in the presence of hydroxyl ions.

The manganate ion, $M\overset{=}{n}O_4$, differs entirely in its properties from the permanganate ion, $M\overset{-}{n}O_4$, just as $\overset{++}{S}n$ differs from $\overset{++++}{S}n$, and $(Fe\equiv\overset{=}{C}_6N_6)$ from $(Fe=\overset{\equiv}{C}_6N_6)$. In the presence of $\overset{+}{H}$ ions, even the concentration existing in pure water, $M\overset{=}{n}O_4$ changes into $M\overset{-}{n}O_4$.

$$3MnO_4 + 4\overset{+}{H} \rightarrow 2M\overset{-}{n}O_4 + \mathbf{H_2MnO_3} + H_2O$$

Hence it is that an alkaline solution of a manganate, by absorption of CO_2 from the atmosphere, is gradually changed to the pink color characteristic of permanganates.

Heptavalent manganese, the highest state of oxidation that can be obtained with this element, is reached only in acid solution by the action of strong oxidizing agents on lower oxidized compounds. In this condition manganese is entirely acidic in nature. The oxid, Mn_2O_7, is a heavy dark-colored oil which parts with its oxygen readily to form compounds of lower oxidation. It is the anhydrid of permanganic acid, $HMnO_4$, a strong acid, all the compounds of which are characterized by a rich purple color, becoming pink in dilute solution.

All compounds of manganese, heated in the oxidizing flame before the blowpipe in a **bead of borax,** or sodium metaphosphate, produce an amethyst color due to the formation of manganic oxids (Mn_2O_3 or Mn_3O_4). If manganese is present in relatively large amounts, the bead is brown and resembles the color given by iron or nickel. (See pages 221 and 232.)

Heated with oxidizing agents, such as $KClO_3$ or with Na_2CO_3 to which a little KNO_3 has been added, all manganese compounds give a green color due to the formation of manganates of the alkali metals.

Boiled with HNO_3 and PbO_2 (or Pb_3O_4), all manganese compounds, soluble under these conditions, give a pink color to the solution, due to the formation of permanganic acid. The color is best observed after allowing the suspended matter to settle.

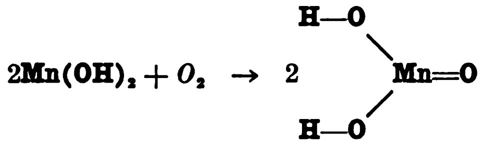
The common **manganese ions** are $\overset{++}{\mathbf{Mn}}$ and $\overset{-}{\mathbf{MnO_4}}$. As the reactions of these ions are of importance, they will be considered more in detail.

The Manganous Ion, $\overset{++}{\mathbf{Mn}}$.

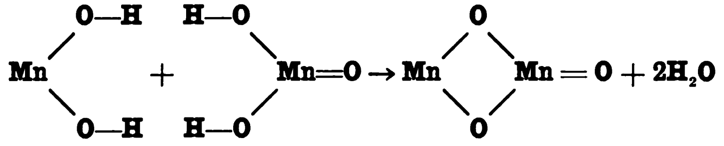
For the $\overset{++}{Mn}$ ion, a solution of any soluble salt will serve. The nitrate, $Mn(NO_3)_2.6H_2O$, is a deliquescent, very soluble salt, melting in its own water of crystallization at temperatures but little above the ordinary.

The **hydroxyl ion, $\overset{-}{\mathbf{OH}}$,** precipitates white $Mn(OH)_2$, insoluble in excess of the precipitant, thus indicating that bivalent manganese possesses no acid-forming properties. Unlike the hydroxids of cobalt, nickel and zinc, it does not form manganese-ammonia ions and, therefore, does not dissolve in NH_4OH. With ammonium salts, however, it forms complex salts of the type, $(NH_4)_2(MnCl_4)$, which is characteristic of ferrous iron, cobalt, nickel, zinc and magnesium as well. For this reason, when the ionization of NH_4OH is repressed by the presence of NH_4Cl in considerable quantities, NH_4OH produces no precipitate of $Mn(OH)_2$.

Manganous hydroxid slowly absorbs oxygen, forming brown manganous acid according to the equation:



This change takes place quite rapidly in hot solutions containing the $\overset{-}{\mathrm{O}}\mathrm{H}$ ion and is immediate in the presence of oxidizing agents. Manganous acid reacts with manganous hydroxid to form brown manganese manganite, which is the oxid Mn_2O_3, according to the equation:



Neither the acid nor the manganite is soluble in NH_4Cl, hence, on standing, a brown precipitate separates from hot solutions of manganous salts made alkaline with NH_4OH, even in the presence of much NH_4Cl.

The **carbonate ion, $\overset{=}{\mathrm{C}}\mathrm{O}_3$**, precipitates white $MnCO_3$ even in the presence of NH_4Cl. In this point manganese differs from cobalt, nickel, zinc, and magnesium. The carbonate is slowly oxidized and hydrolyzed, thus producing the brown precipitate to which reference has already been made.

The **sulfid ion, $\overset{=}{\mathrm{S}}$**, precipitates from neutral and alkaline solutions a hydrated MnS which is flesh-colored. It is exceedingly soluble, even in acetic acid, and, for this reason, the precipitation by H_2S from neutral solutions is not complete because equilibrium ensues.

$$MnCl_2 + H_2S \leftrightarrow \mathbf{MnS} + 2HCl$$

For this reason, the precipitation is best made in alkaline solution by the use of ammonium sulfid.

On boiling with a large excess of $(NH_4)_2S$, the hydrated flesh-colored MnS loses water, turning green as the dehydration proceeds.

The **sulfate ion, $\overset{=}{\mathrm{S}}\mathrm{O}_4$**, causes no precipitate, as the sulfate, $MnSO_4.4H_2O$, is soluble in about 3 parts of H_2O. A sulfate containing $7H_2O$ can be obtained at low temperatures, having the characteristic form of the "vitriols" but it is not the ordinary crystallized salt.

The **chlorid ion, $\overset{-}{\mathrm{Cl}}$**, produces no precipitate, for $MnCl_2.4H_2O$ is soluble in less than its own weight of water. The salt is deliquescent and therefore does not keep well.

The **cyanid ion, $\bar{C}N$,** precipitates white $Mn(CN)_2$, soluble in dilute acids. It dissolves readily in an excess of alkaline cyanid forming a complex cyanid of the type, $K_4(Mn = C_6N_6)$. These manganocyanids correspond to ferrocyanids and cobaltocyanids (see pages 223 and 230), and, unlike the former but like latter, the ion is quite unstable except in the presence of a considerable excess of alkaline cyanid. If this excess be not present, potassium manganocyanid reacts with the manganous cyanid formed by decomposition to give a green precipitate of potassium manganese manganocyanid according to the equation:

$$K_4(Mn = C_6N_6) + Mn(CN)_2 \rightarrow \mathbf{K_2Mn(Mn = C_6N_6)} + 2KCN$$

The precipitate dissolves on the addition of more KCN reversing the reaction.

Manganocyanids, on exposure to the air, slowly oxidize to manganicyanids according to the equation:

$$2K_4(Mn = C_6N_6) + O + H_2O \rightarrow 2K_3(Mn \equiv C_6N_6) + 2KOH$$

or, writing an ionic equation:

$$2(Mn = \overset{=}{C}_6N_6) + O + H_2O \rightarrow 2(Mn \equiv \overset{=}{C}_6N_6) + 2\ \bar{O}H$$

These compounds are no more stable than the manganocyanids and, on acidifying, are entirely decomposed, the manganicyanic acid first formed breaking down as shown by the equation:

$$2H_3(Mn \equiv C_6N_6) \rightarrow 2\mathbf{Mn(CN)_2} + 6HCN + (CN)_2$$

The **ferrocyanid ion, $(\mathbf{Fe = \overset{=}{C}_6N_6})$,** precipitates white $Mn_2(Fe = C_6N_6)$, soluble in acids of fair concentration.

The **ferricyanid ion, $(\mathbf{Fe \equiv \overset{\equiv}{C}_6N_6})$,** precipitates brown $Mn_3(Fe \equiv C_6N_6)_2$, soluble in acids of fair concentration.

The **phosphate ion, $\overset{\equiv}{\mathbf{P}}\mathbf{O}_4$,** precipitates white $Mn_3(PO_4)_2$, soluble even in acetic acid.

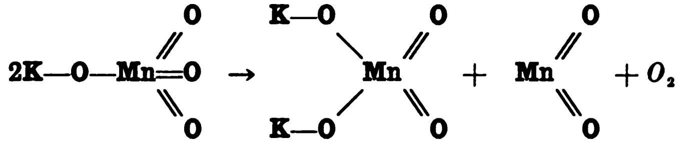
The Permanganate Ion, $\mathbf{M\bar{n}O_4}$.

By the action of strong oxidizing agents in the presence of acids (as already stated, page 216) solutions are obtained which contain the permanganate ion, $M\bar{n}O_4$, as well as $\overset{+}{H}$ ions. Permanganic acid, $HMnO_4$, is, however, entirely unknown out of solution, for every attempt to isolate it results only in the anhydrid, Mn_2O_7, or more often its decomposition products.

Many **salts of permanganic acid** are well known, however. They are all of a dark red color with a greenish iridescence. All are readily soluble, giving purple solutions which change to pink as dilution increases. Inasmuch as the permanganates of the alkali metals give neutral aqueous solutions, it is evident that no hydrolysis takes place and that $HMnO_4$ must be a strong acid.

The alkaline permanganates are by far the most important salts. Potassium and ammonium permanganates are soluble each in about 15 parts of H_2O and separate from solution without water of crystallization. Sodium permanganate, $NaMnO_4.3H_2O$, is much more soluble but cannot be handled as well as salts of other alkalies.

Permanganates, as a class, are such highly-oxidized compounds that they are not very stable, but tend to liberate a portion of their oxygen and break down into compounds of a lower stage of oxidation. Heated to 240°, potassium permanganate, which is the most stable salt, decomposes into the manganate.



In solution, the same change takes place on long standing and a brown precipitate of MnO_2, more or less hydrated, forms. By boiling concentrated solutions of permanganates in the presence of strong alkalies, the reaction is hastened and the presence of the manganate is indicated by the color of the solution. This is evidently the reverse of the reaction by which permanganates are formed. (See page 215.)

The extreme ease with which permanganates liberate oxygen make them the **best of oxidizing agents.** Anything which can be oxidized at all in solution will be oxidized by permanganates. In acid solutions, permangates give up so much oxygen that they are reduced from the heptavalent to the divalent condition and form manganous salts with the acid present. From two molecules of permanganate, five atoms of nascent oxygen are liberated as the equation shows:

$$2HMnO_4 \rightarrow H_2O + 2MnO + 5O =$$

In the presence of H_2SO_4, MnO dissolves to form manganous sulfate, in HCl, $MnCl_2$, etc. (See also page 49.)

In alkaline solution, only three atoms of nascent oxygen are obtained from two molecules of permanganate, the manganese changing from the heptavalent to the tetravalent condition only, and a brown precipitate of MnO_2, more or less hydrated, is formed.

$$2KMnO_4 + H_2O \rightarrow \mathbf{2MnO_2} + 2KOH + 3O=$$

The metathetical reactions of permanganates are of little importance since all the salts are soluble. For this reason:

The **barium ion, $\overset{++}{Ba}$,** added to solutions containing the **permanganate ion, $\overset{-}{MnO}_4$,** gives no precipitate.

The **silver ion, $\overset{+}{Ag}$,** gives no precipitate, except in concentrated solutions, for $AgMnO_4$ is soluble in about 100 parts of H_2O at ordinary temperatures.

Group 8.

Iron 55.9;	**Cobalt 59;**	**Nickel 58.7;**
Ruthenium 101.7;	Rhodium 103;	Palladium 106.5;
Osmium 191;	Iridium 193;	**Platinum 194.8.**

This group is constituted somewhat differently from the other groups in that its members occur in triplets instead of singly. The free elements are typically metallic. In combination they act as weak base-formers, although the first member of each triplet may act as an acid-forming element when highly oxidized. What might be called the characteristic valence of eight is shown by ruthenium and osmium only, but, even with these as with the other members of this group, lower valences are more often exhibited. The first triplet, iron, cobalt and nickel, are the only ones occurring in any quantity. Platinum will be considered in detail, also, because of its importance in the laboratory.

IRON (Ferrum). Fe — 55.9.

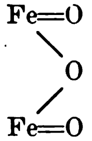
Metallic iron, when pure, is almost silver-white in color and melts above 1800°. Commercial iron always contains impurities which darken its color and lower its melting-point very considerably. It is the most magnetic of metals. It unites readily with oxygen at high temperatures, forming the magnetic oxid, Fe_3O_4. At ordinary temperatures it is permanent in dry air but, in the presence of moisture and CO_2, it "rusts" (see later).

Iron is very soluble in dilute acids, even in acetic and much weaker acids, forming salts in which the metal is bivalent, or in the ferrous condition. The passage into the ionic condition is accompanied by the liberation of energy, hence iron salts are not easily reduced to the metal. Only in the "dry way" can this be accomplished. On the other hand, iron will precipitate silver, mercury, bismuth, copper, gold and platinum from solutions of their salts.

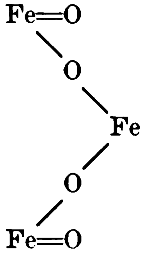
Two **oxids** are known from which, by treatment with acids, two series of salts may be derived. On treatment with acids the magnetic oxid, Fe_3O_4, forms two-thirds ferric and one-third ferrous salt, hence its formula is written as shown below:

$Fe=O$

Ferrous oxid.



Ferric oxid.



Magnetic oxid.

Ferrous salts are usually light green or white in color, with a slight tendency toward hydrolysis, for bivalent iron acts as a stronger base-forming element than many other heavy metals. The salts of the ordinary acids are often soluble but the solutions become turbid because of oxygen in the atmosphere and a precipitate of ferric oxysalts forms.

Ferrous salts pass into the corresponding trivalent ferric compounds on exposure to the atmosphere and, more rapidly, under the influence of oxidizing agents. By the action of the stronger reducing agents, the reverse process is accomplished and ferric salt becomes ferrous.

Ferric compounds are usually of a red or deep yellow color, the salts of the common acids being soluble, hydrolyzing to a very great degree and tending to form insoluble basic or oxysalts which require the presence of free acid to keep them in solution. Ferric iron is much less basic than ferrous iron yet shows no acid-forming properties. When the valence rises to six, iron acts as an acid-forming element. The formula of potassium ferrate, K_2FeO_4, shows its analogy to K_2MnO_4, K_2CrO_4 and K_2SO_4.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all iron compounds are reduced to the metal. The temperature is usually not high enough to make the metal sufficiently liquid to collect in a globule but a black magnetic crust or fine gray particles are formed instead.

Heated in a **borax-bead** before the blowpipe in the oxidizing flame, iron salts give a yellow-to-brown color when hot, becoming much lighter when cold. In the reducing flame, the bead is green.

Of the **iron ions** the ferrous ion, $\overset{++}{Fe}$, and the ferric ion, $\overset{+++}{Fe}$, are the most important. Besides these kathions iron is a component of several anions. The ferrate ion, $\overset{=}{\mathrm{Fe}}\mathrm{O}_4$, is of little importance. Many complex anions are known of which the ferrocyanid ion, $(\mathrm{Fe}=\overline{\mathrm{C}}_6\mathrm{N}_6)$, and ferricyanid ion, $(\mathrm{Fe}\equiv\overline{\mathrm{C}}_6\mathrm{N}_6)$, are the best known.

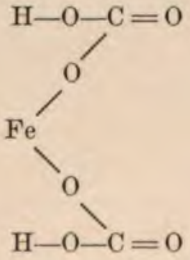
The Ferrous Ion, $\overset{++}{\mathrm{Fe}}$.

For the reactions of the $\overset{++}{\mathrm{Fe}}$ ion, a solution of the chlorid or sulfate are satisfactory.

The **hydroxyl ion, $\overline{\mathrm{OH}}$,** precipitates from solutions of pure ferrous salts protected from all oxidizing agents, white $\mathrm{Fe(OH)_2}$, readily soluble in $\mathrm{NH_4Cl}$, as are the hydroxids of cobalt, nickel, manganese and zinc. Unless special precautions are taken, however, the precipitate is dark green in color, owing to partial oxidation which may progress until red ferric hydroxid is finally produced. As the oxidation increases, the solubility in $\mathrm{NH_4Cl}$ and the similarity to the zinc group in general decreases.

The **carbonate ion, $\overset{=}{\mathrm{CO}}_3$,** in the absence of air, precipitates white $\mathrm{FeCO_3}$, otherwise a green partially-oxidized product. As the oxidation increases, hydrolysis increases until finally ferric hydroxid is precipitated and carbonic acid formed which, for the most part, separates into $\mathrm{CO_2}$ and $\mathrm{H_2O}$.

Ferrous carbonate dissolves in water containing $\mathrm{CO_2}$, forming the acid carbonate,



In this condition iron exists in chalybeate springs and, on exposure to the air, is precipitated as ferric hydroxid.

The "rusting" of iron may be explained by these same reactions. Carbonic acid attacks the metal, liberating hydrogen and forming ferrous acid-carbonate which oxidizes to ferric acid-carbonate. The latter compound hydrolyzes completely into ferric hydroxid and the original amount of carbonic acid. Ferric hydroxid, more or less dehydrated, is "iron rust."

The **sulfid ion, $\overset{=}{\mathrm{S}}$,** precipitates black FeS, readily soluble in acids, even in acetic acid, but insoluble in alkalies or their sulfids. Because of these solubility relations, H_2S passed into an acid solution causes no precipitate. From a neutral solution, FeS is only partially precipitated. An equilibrium ensues which may be expressed by the equation:

$$\mathrm{FeCl_2 + H_2S \leftrightarrow \mathbf{FeS} + 2HCl}$$

The **sulfate ion, $\overset{=}{\mathrm{S}}\mathrm{O}_4$**, produces no precipitate, as ferrous sulfate is soluble in about its own weight of water at ordinary temperatures. From solutions it separates with 7 molecules of water of crystallization in the form which is characteristic of the "vitriols." As "green vitriol" or "copperas," it finds many industrial uses.

The **chlorid ion, $\bar{\mathrm{C}}\mathrm{l}$,** produces no precipitate as the ferrous halids are all soluble. From aqueous solution $FeCl_2.4H_2O$ separates and will dissolve again in less than its own weight of water at ordinary temperatures.

The **cyanid ion, $\bar{\mathrm{C}}\mathrm{N}$,** precipitates brown $Fe(CN)_2$, appreciably soluble only in concentrated acids. It dissolves in an excess of alkaline cyanid, however, forming a complex cyanid of the type, $K_4(Fe=C_6N_6)$ which separates into $\overset{+}{\mathrm{K}}$ and $(\mathrm{Fe}=\overset{==}{\mathrm{C}}_6\mathrm{N}_6)$ ions. The ferrocyanid ion is one of the most stable of all complex ions, even in very dilute solutions it decomposes into the simple ions to such a slight extent that the concentration of $\overset{++}{\mathrm{Fe}}$ ions is inappreciable and no reactions of ferrous salts can be obtained. The ion is stable under very varying conditions. On acidifying a solution of a ferrocyanid, it is not decomposed but a compound of the composition $H_4(Fe=C_6N_6)$ may be isolated. In solution, this body ionizes to about the same degree as sulfuric acid into $\overset{+}{\mathrm{H}}$ ions and $(\mathrm{Fe}=\overset{==}{\mathrm{C}}_6\mathrm{N}_6)$ ions. Therefore, it is known as ferrocyanic acid, detailed consideration of which is given under a separate heading. (See page 130, also 127.)

The **phosphate ion, $\overset{\equiv}{\mathrm{P}}\mathrm{O}_4$,** precipitates light-green $Fe_3(PO_4)_2$, readily soluble in the stronger acids.

The **ferrocyanid ion, $(\mathrm{Fe}=\overset{==}{\mathrm{C}}_6\mathrm{N}_6)$,** causes a white precipitate if all oxidizing agents be excluded. Ordinarily, the precipitate is light blue, due to partial oxidation. The composition of the substance under either condition will vary according to the relative amounts of the reagents present, being $Fe_2(Fe=C_6N_6)$ if an excess of $\overset{++}{\mathrm{Fe}}$ ions be present, and $FeK_2(Fe=C_6N_6)$ if an excess of $(\mathrm{Fe}=\overset{==}{\mathrm{C}}_6\mathrm{N}_6)$ ions be present. Either body is insoluble in dilute acids but is decomposed by alkalies with the separation of ferrous hydroxid and an alkaline ferrocyanid.

The **ferricyanid ion, $(\mathrm{Fe}\equiv\overset{\equiv}{\mathrm{C}}_6\mathrm{N}_6)$,** causes a dark blue precipitate of ferrous ferricyanid, $Fe_3(Fe\equiv C_6N_6)_2$, or "Turnbull's blue." It is insoluble in acids but is decomposed by boiling alkalies into ferrous hydroxid and alkaline ferricyanid. Since ferricyanids in alkaline solution are energetic oxidizing agents, ferric hydroxid is precipitated and alkaline ferrocyanid formed, in part, at least. (See pages 131 and 132.)

Because of the great intensity of color produced, alkaline ferricyanids offer a very delicate test for the ferrous iron, a test not ordinarily confused by the presence of any other substance. Since ferrous salts oxidize so readily, the test should always be made on a fresh solution of the original substance.

The **thiocyanate ion, $\overset{-}{\mathrm{SCN}}$,** is without effect on a solution containing only $\overset{++}{\mathrm{Fe}}$ ions.

The Ferric Ion, $\overset{+++}{\mathrm{Fe}}$.

For the reactions of the $\overset{+++}{\mathrm{Fe}}$ ion, a solution of the chlorid serves best.

The **hydroxyl ion, $\overset{-}{\mathrm{OH}}$,** precipitates red $Fe(OH)_3$ which loses water in various proportions and finally becomes red ferric oxid, Fe_2O_3. The hydroxid, and oxid also if formed by gentle heating, are readily soluble in acids, like hydroxids and oxids generally, but, after strong ignition, Fe_2O_3 is very resistant to all ordinary agents. By fusing with acid sulfates, however, it is changed to ferric sulfate by the nascent SO_3 (see page 188) and so may be obtained in solution. The hydroxid shows no acid properties, hence it is insoluble in alkaline solutions. Ferric hydroxid shows a strong tendency toward the formation of pseudo-solutions which are of a deep red color.

In the presence of tartaric and citric acids, sugar and other organic substances containing the hydroxyl radicle, ferric hydroxid is not precipitated, owing to the formation of complex bodies which do not form $\overset{+++}{\mathrm{Fe}}$ ions. Hence it is necessary that organic matter in general be removed from solution before the attempt is made to precipitate ferric iron. Ignition offers a satisfactory method of removing organic matter.

The **carbonate ion, $\overset{=}{\mathrm{CO}}_3$,** forms, possibly, ferric carbonate, but, owing to the weakness of ferric hydroxid and carbonic acid as well, it is completely hydrolyzed, CO_2 is liberated and $Fe(OH)_3$ is precipitated.

The **sulfid ion, $\overset{=}{\mathrm{S}}$,** does not precipitate ferric sulfid, for this compound, formed only in the "dry way," is completely hydrolyzed on treatment with water. If H_2S is passed into a solution of $FeCl_3$, for instance, if ferric sulfid formed, HCl would be formed as well. By hydrolysis of the sulfid, ferric hydroxid would be formed which would dissolve in the HCl produced to give the original salt, $FeCl_3$. Hence no such action is apparent.

Hydrogen sulfid is a reducing agent, however, and, as such, changes the ferric ions into ferrous ions, liberating sulfur at the same time as the equations indicate:

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + \mathbf{S}$$
$$2\overset{+++}{Fe} + H_2S \rightarrow 2\overset{++}{Fe} + 2\overset{+}{H} + \mathbf{S}$$

In the presence of acids, the color changes from yellow to light green and the precipitated sulfur renders the solution turbid. Since FeS is insoluble in water and alkalies, if the sulfid ion is introduced in excess into an alkaline solution of a ferric salt, the excess of $\overset{=}{S}$ ions will react with the $\overset{++}{Fe}$ ions, formed during the reduction, and black FeS will be precipitated.

The **sulfate ion, $\mathbf{\overset{=}{SO}_4}$**, produces no precipitate, as $Fe_2(SO_4)_3$ is very soluble. It deliquesces greatly under ordinary conditions and soon absorbs enough moisture to pass into solution.

The **chlorid ion, $\mathbf{\overset{-}{Cl}}$**, causes no precipitate, for $FeCl_3$ is very deliquescent and very soluble, like other ferric halids.

If the normal salt, ferric chlorid (or sulfate or nitrate) be dissolved in water, the solution will have an acid reaction owing to hydrolysis because of the weak basic properties of trivalent iron.

$$FeCl_3 + 3H_2O \leftrightarrow \mathbf{Fe(OH)_3} + 3HCl$$

Because $Fe(OH)_3$ is insoluble, the reaction will continue in the direction toward the right much beyond the point at which equilibrium would result if $Fe(OH)_3$ were soluble. Nevertheless, an equilibrium is produced, the balance being brought about by the opposition of the two reactions; on the one side, hydrolysis tending to produce $Fe(OH)_3$, on the other side, the action of HCl on $Fe(OH)_3$ to produce the original salt. The presence of free acid is indicated by the reaction of the solution to litmus. The presence of the free base by the turbidity of the solution. Since hydrolysis increases with the temperature, the turbidity is increased by boiling.

If the acid be removed in any way as fast as it is formed by hydrolysis, no equilibrium will ensue and the reaction will proceed entirely in the direction from left to right. Barium or other insoluble carbonate serves admirably to remove all free acid, since, by the interaction, carbonic acid is formed which, for the most part, breaks down into CO_2 and H_2O. By continually reducing the concentration of acid, $BaCO_3$ causes complete hydrolysis of the ferric salts of strong acids and the complete precipitation of $Fe(OH)_3$. Salts of aluminum and trivalent chromium act similarly.

The **cyanid ion, $\overset{-}{C}N$,** causes the precipitation of $Fe(OH)_3$, ferric cyanid being unknown. By the union of the hypothetical $Fe(CN)_3$ with 3KCN, a complex cyanid might theoretically be formed, having the formula, $K_3(Fe{\equiv}C_6N_6)$. Such a compound, potassium ferricyanid, is known and may be formed by the oxidation of potassium ferrocyanid. It ionizes into $\overset{+}{K}$ and $(Fe{\equiv}\overset{\equiv}{C}_6N_6)$ ions, the latter being very stable. The corresponding hydrogen compound, $H_3(Fe{\equiv}C_6N_6)$ can be isolated. It separates $\overset{+}{H}$ ions and is therefore known as ferricyanic acid, under which heading it is treated more in detail. (See pages 131, also 127.)

The **phosphate ion, $\overset{\equiv}{P}O_4$,** precipitates yellowish-white $FePO_4$, which, like phosphates generally, is soluble in the stronger mineral acids. Unlike many phosphates it is insoluble in acetic acid, and ferric compounds may be separated from salts of the metals included in Groups III and IV of the scheme of qualitative analysis and from magnesium as well, by the introduction of the $\overset{\equiv}{P}O_4$ ion into solutions acidified with acetic acid.

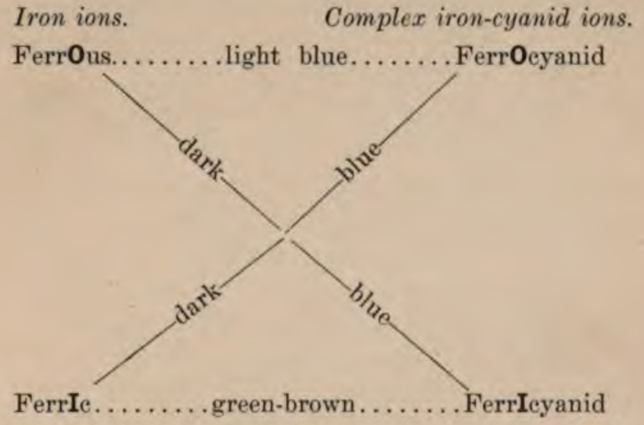
The **acetate ion, $(C_2\overset{-}{H}_3O_2)$,** added to a solution causes no precipitate, for $Fe(C_2H_3O_2)_3$ is soluble. Being the salt of a comparatively weak acid as well as of a weak base, ferric acetate solutions hydrolyze to a great extent, ferric hydroxid showing especial tendency under these conditions to form pseudo-solutions. This fact accounts for the characteristic deep red color of ferric acetate solutions. In a dilute boiling solution, an equilibrium is reached in which approximately two-thirds of all the acetic acid present exists in the uncombined condition. The resulting precipitates, having the proportions indicated by the formula, $Fe(OH)_2(C_2H_3O_2)$, is known as basic ferric acetate. Its appearance is identical with ferric hydroxid, but it is not soluble in solutions containing acetic acid in concentration sufficient to dissolve $Fe(OH)_3$.

The **ferrocyanid ion, $(Fe{=}\overset{\equiv}{C}_6N_6)$,** precipitates dark blue ferric ferrocyanid, $Fe_4(Fe{=}C_6N_6)_3$, Prussian blue. The compound is not affected by concentrated acids, but is decomposed by boiling alkalies with the formation of ferric hydroxid and alkaline ferrocyanid.

Because of the intensity of color produced, the ferrocyanid ion offers a good means of detecting the ferric ion, just as the ferricyanid ion serves to detect the presence of the ferrous ion. The test should be applied to a fresh solution of the original substance, as, otherwise, the ferric ion may be formed by the oxidation of ferrous compounds by the air.

The **ferricyanid ion, $(Fe{\equiv}C_6\overset{\equiv}{N}_6)$,** produces no precipitate, for $Fe(Fe{\equiv}C_6N_6)$ is soluble. The solution of ferric ferricyanid is a deep greenish-brown color, however.

In testing for the presence and condition of iron with the complex iron cyanids, any color except dark blue should be disregarded. A deep blue color is produced whenever ferrous ions are brought together with ferri(c)cyanid ions or ferric ions with ferro(us)cyanid ions, but not when ferrous ions and ferro(us)cyanid ions come together or ferric ions meet with ferri(c)cyanid ions, as the diagram indicates.


Iron ions.
Complex iron-cyanid ions.
Ferr**O**us.........light blue........Ferr**O**cyanid
dark
blue
dark
blue
Ferr**I**c.........green-brown........Ferr**I**cyanid

The **thiocyanate ion, $\overline{SCN}$,** produces no precipitate, for $Fe(SCN)_3$ is very soluble. Undissociated ferric thiocyanate is blood-red in color and thus offers a very delicate test for ferric iron. The color is intensified by an excess of KSCN, which dissociates to a greater degree than $Fe(SCN)_3$, and, therefore, causes the ionization of the latter compound to be repressed, resulting in a larger quantity of the undissociated highly-colored salt.

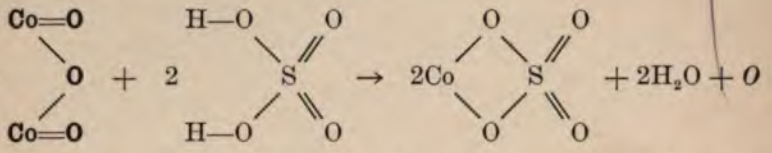
Ferric thiocyanate is soluble in ether and in amyl alcohol, neither of which solvents cause dissociation. By shaking an aqueous solution with ether or amyl alcohol, the $Fe(SCN)_3$ will be collected from the water and the color intensified. (See also pages 129 and 231.)

COBALT. CO — 59.

Cobalt is a comparatively rare, magnetic, malleable metal of a gray color with a slight reddish tint. In many of its properties and in the character of its compounds, it closely resembles iron and nickel.

The metal dissolves slowly in HCl and H_2SO_4 and readily in HNO_3, forming compounds in which the element is divalent. A small amount of energy only is liberated in passing into the ionic condition. For this reason, the metal is precipitated from solutions of its salts by zinc, magnesium, and other elements which liberate greater amounts of energy as they become ions, *i. e.*, pass more readily into the ionic condition.

Cobalt salts are of two types. The cobaltous series, in which the metal is divalent, may be derived from the oxid, CoO. The cobaltic salts, in which the element is trivalent, may be referred to the oxid, Co_2O_3, although, on treatment with acids, oxygen (or its equivalent) is set free and cobaltous salts only are formed.



A third compound with oxygen, Co_3O_4, corresponds to Fe_3O_4 and is the most stable oxid. It is formed when either of the other oxids are heated. On treatment with acids, it acts as does cobaltic oxid and no salts corresponding to it are known.

Cobaltous salts are numerous, well known and generally stable. They are of a yellow or blue color when anhydrous but aqueous solutions and crystals containing water of crystallization are pink. Most salts of the commoner acids are soluble. They hydrolyze but little and resemble very closely the corresponding ferrous salts. Unlike ferric salts which hydrolyze greatly, cobaltous salts are not precipitated as the hydroxid by treating their cold solutions with $BaCO_3$.

Cobaltic compounds are generally unstable under ordinary conditions. Aside from the oxid and hydroxid, no simple salts are definitely known. Possibly some of the halids exist in solution. Several complex salts of trivalent cobalt are stable and well recognized, however. They will be considered in connection with the cobaltous compounds from which they may be derived.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, all cobalt compounds are reduced, leaving a dark magnetic crust.

Heated in the **borax-bead,** all cobalt compounds produce a deep blue color, probably due to the formation of cobalt meta-borate, $Co(BO_2)_2$.

The common **cobalt ion** is $\overset{++}{\mathbf{Co}}$. The trivalent ion, $\overset{+++}{Co}$, is not definitely known. Both divalent and trivalent cobalt form large numbers of complex salts of varying composition, most of which give easily recognized complex ions. Complex cobalt-ammonia salts of two types are known, one of which contains four molecules of NH_3 to one of the metal, the other $6NH_3$. The salts give rise to the following complex ions:

$$\overset{++}{Co}.(NH_3)_4 \qquad \overset{++}{Co}.(NH_3)_6 \qquad \overset{+++}{Co}.(NH_3)_6$$

The NH_3 in these compounds may be replaced more or less completely by H_2O and other molecules; by CN, NO_2, and other radicles; and by Cl and other atoms, giving rise to a great variety of compounds. If the substituting radicle or element is acidic in nature, *i. e.*, ordinarily forms ions carrying negative charges, as $\overline{\text{Cl}}$, $\overline{\text{CN}}$ and $\overline{\text{NO}}_2$, the character of the complex ion changes gradually, one positive charge being removed or a minus charge being added as each successive substitution occurs, as the following series indicates:

$$\overset{+++}{\text{Co}}.\widetilde{(\text{NH}_3)_6},\quad \overset{++}{\text{Co}}.(\text{NH}_3)_5.\dot{\text{NO}}_2,\quad \text{Co}.(\text{NH}_3)_4.2\text{NO}_2,\quad \text{Co}.(\text{NH}_3)_3.3\text{NO}_2,$$
$$\text{Co}.(\text{NH}_3)_2.4\overline{\text{NO}}_2,\quad \text{Co}.(\text{NH}_3).5\overline{\text{NO}}_2,\quad \text{Co}.6\overset{\equiv}{\text{NO}}_2.$$

The last of the above series—the cobalti-nitrite ion—as well as the corresponding cobalticyanid ion, $\text{Co}.6\overset{\equiv}{\text{CN}}$, are well known. By an extension of this principle, all the known ammonia compounds (and their derivatives) of any of the metals may be included in this classification.

For the reactions of the $\overset{++}{\text{Co}}$ ion any soluble salt may be used. The nitrate, $Co(NO_3)_2.6H_2O$ is a red, deliquescent, very soluble salt, melting in its own water of crystallization at temperatures not much above the ordinary. The acetate, $Co(C_2H_3O_2)_2.4H_2O$ effloresces and, therefore, is more readily preserved than other cobalt salts.

The **hydroxyl ion, $\overline{\textbf{OH}}$,** added to a solution containing the cobalt ion, $\overset{++}{\text{Co}}$, precipitates a blue basic salt at first, $\text{Co}(\text{OH})(\text{NO}_3)$ for instance, which, in the presence of more $\overline{\text{OH}}$ ions, changes into the pink $Co(OH)_2$. A high concentration of $\overline{\text{OH}}$ ions causes some cobaltous hydroxid to dissolve, thus showing that it may be forced to display slight acidic properties. In NH_4OH and NH_4Cl it dissolves readily, forming complex ammonia compounds. In the presence of sufficient NH_4Cl, therefore, NH_4OH produces no precipitate owing to the formation of these compounds and to the repression of its ionization as well.

On standing in the air, more rapidly under the influence of oxidizing agents, especially of alkaline hypochlorites or hypobromites or of hydrogen peroxid, cobaltous hydroxid oxidizes to brownish-black cobaltic hydroxid, $Co(OH)_3$.

The **carbonate ion, $\overset{=}{\textbf{CO}}_3$,** causes a pink precipitate consisting of the carbonate and hydroxid in varying proportions. This precipitate does not fall in the presence of ammonium chlorid if $(NH_4)_2CO_3$ is used as the precipitating reagent.

The **sulfid ion, $\overset{=}{\textbf{S}}$,** causes no precipitate in solutions containing an appreciable amount of acid. In neutral, alkaline and in acetic acid solutions, provided they be barely acid in reaction, black CoS is precipitated. Although the precipitation is *prevented* by a very small concentration of $\overset{+}{\mathrm{H}}$ ions, CoS, once precipitated, does not dissolve readily in anything except aqua regia. This phenomenon which is exhibited by NiS, also, is probably due to the existence of a highly insoluble modification into which the sulfids first precipitated immediately change. Although not readily or completely soluble in anything except aqua regia, the precipitated sulfid does dissolve somewhat in most of the dilute acids even in acetic acid and, when moist, is slowly oxidized by the air into $\mathrm{CoSO_4}$.

The **sulfate ion, $\overset{=}{\mathbf{SO}}_4$**, causes no precipitation, for $\mathrm{CoSO_4}$ is readily soluble. From solution it separates with $\mathrm{7H_2O}$ in the crystal form characteristic of the "vitriols."

The **chlorid ion, $\overline{\mathbf{Cl}}$**, causes no precipitate to fall, for $\mathrm{CoCl_2.6H_2O}$ is soluble in 2–3 parts of $\mathrm{H_2O}$.

The **cyanid ion, $\overline{\mathbf{CN}}$**, precipitates reddish-brown $\mathrm{Co(CN)_2}$, insoluble in acids but readily soluble in alkaline cyanids, forming a complex salt of the type $\mathrm{K_4(Co = C_6N_6)}$, similar to potassium ferrocyanid. The complex cobaltocyanid ion, $(\mathrm{Co} = \overset{====}{\mathrm{C}}_6\mathrm{N_6})$, is far less stable than the ferrocyanid ion and, in acid solutions, is entirely broken up into the simple ions. Consequently on acidifying a solution of a cobaltocyanid, $\mathrm{Co(CN)_2}$ is precipitated and HCN set free.

On treating with oxidizing agents, cobaltocyanids are oxidized to cobalticyanids according to the reactions:

$$\mathrm{2K_4(CO = C_6N_6) + O + H_2O \rightarrow 2K_3(Co \equiv C_6N_6) + 2KOH}$$
$$8\overset{+}{\mathrm{K}} + 2(\mathrm{Co} = \overset{====}{\mathrm{C}}_6\mathrm{N_6}) + \mathrm{O} + \mathrm{H_2O} \rightarrow 6\overset{+}{\mathrm{K}} + 2(\mathrm{Co} \equiv \overset{\equiv}{\mathrm{C}}_6\mathrm{N_6}) + 2\overset{+}{\mathrm{K}} + 2\ \mathrm{O}\overline{\mathrm{H}}$$

which simplifies to

$$2(\mathrm{Co} = \overset{====}{\mathrm{C}}_6\mathrm{N_6}) + \mathrm{O} + \mathrm{H_2O} \rightarrow 2(\mathrm{Co} \equiv \overset{\equiv}{\mathrm{C}}_6\mathrm{N_6}) + 2\ \mathrm{O}\overline{\mathrm{H}}$$

Cobalticyanids are very similar to ferricyanids. The ion, $(\mathrm{Co} \equiv \overset{\equiv}{\mathrm{C}}_6\mathrm{N_6})$, is much more stable than the ion, $(\mathrm{Co} = \overset{====}{\mathrm{C}}_6\mathrm{N_6})$. It is not decomposed in acid solutions and, on acidifying a solution of a cobalticyanid, neither HCN nor cobaltic cyanid are formed. From the solution a compound may be isolated having the composition indicated by the formula, $\mathrm{H_3(Co \equiv C_6N_6)}$, which separates $\overset{+}{\mathrm{H}}$ ions and, therefore, is to be considered as cobalticyanic acid. The alkali salts are soluble and give with the ions of the heavy metals characteristic precipitates. The compounds of cobalticyanic acid are not of importance, however, and will not be further considered.

The **nitrite ion, $\mathbf{N\bar{O}_2}$**, produces no precipitate in dilute solution, for cobaltous nitrite is soluble. In concentrated solutions, acidified with acetic acid (but not with any mineral acid), the nitrous acid formed oxidizes $Co(NO_2)_2$ to $Co(NO_2)_3$, which will then unite with KNO_2 (but not $NaNO_2$) to form a complex salt, $K_3(Co\equiv(NO_2)_6)$, which is yellow and fairly insoluble. Any salt of nickel formed under the same conditions is readily soluble, hence this reaction offers a means of separating these two metals. This separation requires several hours' standing, however, and should be repeated once again on the filtrate if a considerable quantity of cobalt is present.

The **ferrocyanid ion, $\mathbf{(Fe=\overset{\equiv}{\bar{C}}_6N_6)}$**, causes a drab precipitate of very varying composition, approximating more or less closely to $Co_2(Fe=C_6N_6)$. It is insoluble in dilute acids, but soluble in NH_4OH.

The **ferricyanid ion, $\mathbf{(Fe\equiv\overset{\equiv}{C}_6N_6)}$**, causes a slimy reddish precipitate, $Co_3(Fe\equiv C_6N_6)_2$, insoluble in dilute acids and in NH_4OH.

The **thiocyanate ion, $\mathbf{S\bar{C}N}$**, causes no precipitate, for $Co(SCN)_2$ is very soluble. In concentrated solutions of a thiocyanate, however, complex salts are formed which have a beautiful blue color. They are soluble and more stable in amyl alcohol than in water. In the latter solvent, on dilution, the complex salt is decomposed into the simple salts. Inasmuch as nickel does not form a corresponding compound, a means of detecting traces of cobalt in the presence of large quantities of nickel is here presented. To the solution to be tested 5–10 grams of solid NH_4SCN is added and the solution then thoroughly shaken with 5–10 ccm. of amyl alcohol. If cobalt is present, the alcohol layer will be colored blue.

If ferric iron is present, $Fe(SCN)_3$ (see page 227) will form, the blood-red color of which may mask the test since ferric thiocyanate is also soluble in amyl alcohol. On shaking the alcohol layer with a solution of Na_2CO_3, the iron will be precipitated while the cobalt will not and the blue color will remain in the alcohol.

The **phosphate ion, $\mathbf{\overset{\equiv}{P}O_4}$**, precipitates pink $Co_3(PO_4)_2$, soluble in dilute acids, even in acetic acid.

NICKEL. Ni — 58.7.

Nickel is a malleable, slightly magnetic metal. It is almost silver-white in color and is stable in the air. It closely resembles cobalt in the character of its compounds.

The metal dissolves slowly in HCl and H_2SO_4 and readily in HNO_3, forming compounds in which the element is divalent. The passage into the ionic condition is accompanied by the liberation of a small amount of energy and the metal may be precipitated from solutions of its salts by metallic zinc.

Two **oxids** of nickel are known, the green divalent nickelous oxid, NiO, and the black trivalent nickelic oxid, Ni_2O_3.

All **nickel salts** are formed from the lower oxid. The series is characterized by a green color in solution and when containing water of crystallization, the color changing to yellow as the substances become anhydrous. Many of the salts of the commoner acids are soluble and in solution hydrolyze but little, showing that nickel, like divalent metals in general, acts as a stronger base-forming element than trivalent metals. For this reason, nickel cannot be precipitated as the hydroxid by adding $BaCO_3$ to cold solutions of its salts.

No trivalent nickel compounds are known except the hydroxid, $Ni(OH)_3$.

Heated before the **blowpipe** with Na_2CO_3 on charcoal, nickel compounds are reduced to the metal, forming a dark-gray crust which is slightly magnetic.

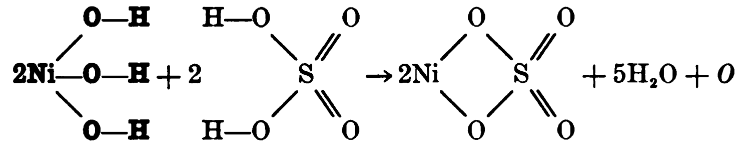
Heated in a **borax-bead** in the oxidizing flame, nickel produces a yellowish-brown color very like that given by iron. In the reducing flame, the bead turns gray and becomes opaque, owing to the presence of fine particles of the metal. The borax-bead can hardly be considered as a decisive test for nickel, however.

The **nickel ion, $\overset{++}{\text{Ni}}$,** is best known. Complex ammonia and cyanogen ions are recognized.

For the reactions of the $\overset{++}{\text{Ni}}$ ion, any soluble simple salt will serve. The nitrate, $Ni(NO_3)_2.6H_2O$, is soluble in about 2 parts of H_2O.

The **hydroxyl ion, $\overset{-}{\text{OH}}$,** precipitates apple-green $Ni(OH)_2$, insoluble in an excess, thus indicating that nickel does not show acid properties. In NH_4OH and in NH_4Cl it is readily soluble, forming a number of complex ammonia compounds similar to some of the cobalt compounds. For this reason, NH_4OH (or $(NH_4)_2CO_3$) causes no precipitate in the presence of NH_4Cl.

In the presence of oxidizing agents, especially alkaline hypochlorites and hypobromites (but not of hydrogen peroxid—distinction from cobalt, see page 229), black $Ni(OH)_3$ is formed. In alkaline solutions, ferricyanids act as oxidizing agents and produce the same product on boiling. Nickelic hydroxid dissolves readily in acids, forming divalent nickel salts and liberating oxygen or its equivalent. (See page 228.)



The **carbonate ion, $\overset{=}{\mathrm{CO}}_3$**, causes an apple-green precipitate, varying in composition, consisting of a mixture of $Ni(OH)_2$ and $NiCO_3$.

The **sulfid ion, $\overset{=}{\mathrm{S}}$**, precipitates black NiS from solutions neutral, alkaline or barely acid with acetic acid. In the presence of a higher concentration of $\overset{+}{H}$ ions and of salts of tartaric and other organic acids, no precipitate falls, the solution merely turning dark. An excess of $(NH_4)_2S$ exerts a similar action, precipitating part only of the NiS and giving a brown filtrate. When once precipitated, however, NiS is not appreciably soluble in acids or in any of these other reagents but shows the same phenomena as CoS. (See page 229.)

The **sulfate ion, $\overset{=}{\mathrm{SO}}_4$**, causes no precipitate, as nickel sulfate is soluble in 2–3 parts of H_2O. From solution it crystallizes with $7H_2O$ in the crystal form characteristic of the "vitriols."

The **chlorid ion, $\overset{-}{\mathrm{Cl}}$**, causes no precipitate, as $NiCl_2.6H_2O$ is soluble in less than two parts of H_2O.

The **cyanid ion, $\overset{-}{\mathrm{CN}}$**, precipitates green $Ni(CN)_2$, insoluble in dilute acids. In an excess of an alkaline cyanid, it is readily soluble, forming a complex cyanid of the type, $K_2Ni(CN)_4$, which forms the complex ion, $(Ni\overset{=}{C}_4N_4)$. In the presence of $\overset{+}{H}$ ions, it is unstable and decomposes entirely into the simple ions, $\overset{++}{Ni}$ and $\overset{-}{CN}$. By treating the complex nickel cyanid with bromin or other oxidizing agents, it is not oxidized to a complex salt of trivalent nickel, as is the case with the corresponding cobalt salt, but it is decomposed according to the equation:

$$K_2Ni(CN)_4 + 8Br \rightarrow 2KBr + NiBr_2 + 4CNBr$$

In the presence of NaOH or KOH, $Ni(OH)_2$ is formed and is oxidized by the bromin to $Ni(OH)_3$, which is precipitated.

$$2\mathbf{Ni(OH)}_2 + 2Br + 2NaOH \rightarrow 2\mathbf{Ni(OH)}_3 + 2NaBr$$

By this means a separation of cobalt and nickel may be effected, since, under similar treatment, a soluble cobalticyanid is formed. (See page 230.)

The **ferrocyanid ion, $(\mathrm{Fe}=\overset{\equiv}{\mathrm{C}}_6\mathrm{N}_6)$**, precipitates light green

$Ni_2(Fe=C_6N_6)$, insoluble in dilute acids but soluble in NH_4OH, forming complex nickel-ammonia compounds.

The **ferricyanid ion, $(\mathbf{Fe\equiv\overline{\overline{\overline{C}}}_6N_6})$,** precipitates olive-brown $Ni_3(Fe\equiv C_6N_6)_2$, insoluble in dilute acid, but soluble in NH_4OH, forming complex nickel-ammonia compounds. Since cobalt ferricyanid is insoluble in NH_4OH, this offers a most satisfactory method of separating nickel from cobalt. (See page 231, also 268.)

The **thiocyanate ion, $\mathbf{S\overline{C}N}$,** causes no precipitate and gives no color to the solution.

The **phosphate ion, $\mathbf{\overline{\overline{\overline{PO}}}_4}$,** precipitates apple-green $Ni_3(PO_4)_2$, soluble in acids, even in dilute acetic acid.

PLATINUM. Pt — 194.8.

Platinum is a heavy, grayish-white, malleable metal, melting at 1770°, a temperature somewhat higher than the flame of an ordinary Bunsen burner. It resembles gold in many of its properties. Like the latter element, it does not tarnish in the atmosphere at any temperature and does not dissolve in any acid. Since it is readily acted upon by the halogens, it does dissolve in aqua regia, forming hydrochlorplatinic acid, H_2PtCl_6. Platinic chlorid, $PtCl_4$, is undoubtedly a transition product (see later).

The finely divided metal obtained by the reduction of its salts—"platinum black"—or by their decomposition by heat—"platinum sponge"—has the power of absorbing large quantities of hydrogen, oxygen and other gases. Since these substances are liberated in a very much more reactive (nascent) condition (see page 40), the presence of finely divided platinum is a very great aid in certain chemical reactions.

Platinum does not pass voluntarily into the ionic condition but requires that energy be expended to make it assume the electric charge. Like gold it stands very low in the Potential Series, hence from solutions of platinum salts, the element is precipitated by the introduction of any of the other common metals.

With oxygen, platinum does not unite directly but, by indirect methods, two compounds with this element may be obtained.

Platinum monoxid, PtO, together with the divalent platinous salts derived from it, are of little importance and, in general, resemble the corresponding higher oxidized compounds which are generally of a much lighter color.

The **tetravalent platinic salts,** derived from the dioxid, PtO_2, are generally soluble and of a yellowish-brown color. They are more stable than the corresponding auric salts, as is indicated by the facts that oxalic acid and ferrous salts cause no reduction at ordinary temperatures in acid solutions, although long boiling with ferrous salts in neutral solutions causes a precipitation of the metal. Stannous chlorid does not precipitate metallic platinum but causes the formation of soluble platinous salts. Hydriodic acid accomplishes a similar reduction to the platinous condition but hydrogen sulfid is without effect. (See page 89.)

On ignition, all platinum salts are decomposed into the metal and, when heated before the **blowpipe** on charcoal with Na_2CO_3, they leave behind a dry infusible gray powder, which shows metallic lustre when rubbed in a mortar.

Simple platinum salts are only infrequently met with, owing to a very strong tendency toward the formation of complex bodies by the addition of many other substances. To illustrate: Platinic chlorid, $PtCl_4$, which separates into the simple $\overset{++++}{Pt}$ and $\overset{-}{Cl}$ ions, is but little known because it unites so readily with hydrogen chlorid (or, analogously, with other chlorids) to form the compound hydrochlorplatinic acid, H_2PtCl_6, which separates, along with hydrogen ions, the chlorplatinate ion, $\overset{=}{PtCl_6}$.

Salts of hydrochlorplatinic acid are of considerable importance. The potassium salt, K_2PtCl_6, and the ammonium salt, $(NH_4)_2PtCl_6$, dissolve to some extent in water (see pages 74 and 78) but they are highly insoluble in dilute alcohol. They are frequently made use of for the separation of ammonium and potassium radicles from solution.

The **hydroxyl ion, $\overset{-}{OH}$,** added to an acid solution containing tetravalent platinum, does not precipitate platinic hydroxid, but forms instead the alkali chlorplatinate. Platinic hydroxid, when obtained under carefully prescribed conditions, is found to act either as a base or an acid, dissolving either in acids or in bases, like gold hydroxid.

The **sulfid ion, $\overset{=}{S}$,** added to a solution containing tetravalent platinum, decomposes the chlorplatinate ion, $\overset{=}{PtCl_6}$ and precipitates black PtS_2, which is insoluble in all acids. It dissolves in aqua regia, however. Platinic sulfid unites with alkaline sulfids to form soluble thioplatinates similar to thiostannates (see page 141). In the scheme of qualitative analysis, therefore, platinum appears in the tin group.

The Care of Platinum Ware.

Although platinum is one of the most resistant of metals, it is incorrect to assume that it may be subjected to the action of all chemical reagents under all conditions without injury. At ordinary temperatures only aqua regia and the halogens act on it, but, at higher temperatures, many other substances have a very appreciable action. Alkaline hydroxids, sulfids and cyanids in the state of fusion all attack it, although alkaline carbonates and borates are without effect. At high temperatures, iodin, sulfur, phosphorus and arsenic react vigorously, and most metals, except iron, form readily fusible alloys. Carbon is not without action on highly heated platinum and vessels of this metal should never be ignited over a luminous flame which deposits soot, *i. e.*, carbon, on a cold object introduced into it.

Not alone must the heating of any of these substances in a platinum vessel be avoided, but care should be exercised that none of these substances shall be formed by the interaction at high temperatures of substances which are themselves harmless. Salts of the metals (especially of silver, mercury, lead, bismuth, tin, zinc, arsenic and antimony) or sulfates or phosphates should never be heated with reducing matter, for the reduction products may completely ruin any platinum vessel in which the ignition takes place.

The physical condition of platinum is a prominent factor in influencing the action of reagents upon it. Platinum ware should always be kept smooth, clean and polished. Should it become stained or tarnished, it should be boiled with dilute nitric acid, or it may be fused with borax and afterwards digested with hot dilute nitric acid. Platinum may be polished conveniently by rubbing between the fingers with fine sea-sand.

PART III

ANALYTICAL

SYSTEMATIC ANALYSIS.

The systematic analysis of any solid substance consists of three parts: the *Preliminary Examination*, as given pages 243–247, the *Basic Analysis*—testing for kathions or metallic elements—as given pages 248–273, the *Acid Analysis*—testing for anions or acid radicles—as given pages 275–309.

The **Preliminary Examination** is made on small portions of the original solid substance. It should rarely be omitted since it takes but a few minutes and, if the substance is homogeneous (*i. e.,* is not a mixture) and is fairly simple, the results of a preliminary examination may render testing unnecessary.

The **Basic Analysis** is the systematic examination to determine the presence or absence of ions of the more commonly occurring metals. The tests consist entirely of reactions performed in the "wet way," thus requiring that the original substance be obtained in solution. It is pulverized, therefore, and the action of the following solvents is tried in the order given.

Water. Boil about 1 gram of the finely powdered substance with 10–20 ccm. of distilled water. If the substance is readily and completely soluble, proceed at once to the Basic Analysis. If it does not dissolve apparently, evaporate 1–2 ccm. of the water extract in platinum to see whether anything has gone into solution. If an appreciable residue is left on the platinum, continue the extraction of the original substance with fresh portions of boiling water as long as anything continues to dissolve. If the substance is insoluble in water, try the action of—

Hydrochloric Acid. Warm the residue left after extraction with water with dilute HCl. If the substance dissolves readily, continue the addition of HCl, if necessary, until no residue is left and treat the solution at once as directed under Filt. 1 of the Basic Analysis; for Group I, Div. A cannot be present if the substance is soluble without residue in HCl. If the substance is not readily soluble in the dilute acid, try the action of concentrated HCl and evaporate a portion of the liquid in platinum to see if anything dissolves. If the substance is insoluble, decant the HCl, wash the residue twice with a little water and decant the washings. Then try the action of—

Nitric Acid. Treat the residue insoluble in water and HCl, first, with boiling dilute HNO_3 and, secondly, if necessary, with concentrated HNO_3 just as in the extraction with HCl. If the substance is soluble in HNO_3, heat the solution to boiling and add concentrated HCl as long as brown fumes or the odor of chlorin is evolved. The formation of a precipitate on the addition of HCl indicates the presence of Group I, Div. A.

By the interaction of HCl with HNO_3 (see page 43), the latter is entirely removed from solution. This is necessitated by the fact that HNO_3 oxidizes H_2S to free sulfur or to H_2SO_4. For this reason its presence in solution would interfere seriously with the Basic Analysis, preventing the precipitation of sulfids of the metals of Group I and possibly causing the precipitation of sulfates of

Group IV. (For these same reasons, other oxidizing agents, if present, interfere with the analysis. This method of boiling with concentrated HCl serves to remove all objectionable oxidizing agents, however.) When further addition of HCl causes no further liberation of brown fumes, evaporate nearly to dryness to remove the excess of acid. Dilute with hot water and, if the solution becomes turbid on dilution, add sufficient HCl to clear it. Filter, if necessary, from any Group I, Div. A precipitate. Examine this precipitate for Ag, Hg and Pb as directed under Prec. 1, page 250. Treat the filtrate as directed under Filt. 1, page 252. If the substance does not dissolve in concentrated HNO_3, try the action of—

Aqua Regia. Add concentrated HCl to the concentrated HNO_3 and warm. If the substance dissolves, remove the HNO_3 from solution and proceed as directed in the preceding paragraphs devoted to the extraction with HNO_3.

Original Solution. The solution thus prepared for systematic analysis, obtained with or without the use of acids, is known as the *original solution.*

In the analysis of complex mixtures, the preceding treatment may result in the solution of one or more components of the mixture by each of the different solvents used. When partial solutions of the original substance are thus obtained, it is preferable to analyze each portion separately; for, by so doing, a better idea may be obtained of the acid which is united to any given base present in the mixture. If, however, it is found that the separate extracted portions may be poured together without producing a precipitate, they may be mixed and the whole treated as the original solution after the removal of nitric acid as previously directed.

During the treatment with HCl in making the original solution, indication is frequently obtained of the presence of certain acids. When carbonates, sulfids, sulfites, thiosulfates, cyanids, nitrites, etc., are treated with HCl, gases (CO_2, H_2S, SO_2, HCN, N_2O_4) are usually liberated which may be recognized by their characteristic odors or detected by the regular methods. These indications should not be overlooked and, if an effervescence is noted, the gas liberated should be determined in every case.

In treating with HNO_3, the presence or absence of brown fumes denoting oxidization should also be noted.

Metals and **alloys** generally should be dissolved in HNO_3, for treatment with HCl may cause the loss of $AsCl_3$, H_2S, PH_3, etc., which are volatile. Phosphorus and sulfur, present in an alloy, are liberated as H_2S and PH_3 on treatment with an acid but are immediately oxidized by HNO_3 to non-volatile compounds:—free sulfur, H_2SO_4, H_3PO_4, etc. If gold, platinum, tin or antimony are present, the alloy will not dissolve without residue in HNO_3; for the first two metals are insoluble and the last two form meta-stannic acid, H_2SnO_3, and antimony pentoxid, Sb_2O_5, respectively, compounds quite insoluble in nitric acid as well as in water. The other compounds of the alloy will readily pass into the solution which should then be treated as previously directed for the removal of HNO_3 and then tested for bases in the regular way. None of the acid-forming elements need be tested for, except sulfur, phosphorus, arsenic, silicon and carbon.

The residue insoluble in HNO_3 should be washed by decantation and then digested with concentrated HCl for 10–15 minutes at the boiling temperature.

Add an equal volume of water and again heat to boiling. This treatment should dissolve most of the tin and antimony and these elements may be detected in the decanted solution in the regular way by passing H_2S and diluting somewhat. The residue insoluble in HCl should be treated with aqua regia, when gold and platinum will dissolve and may be detected in the solution in the usual way. Should any residue still remain, fuse with NaOH and sulfur as directed later under the treatment of insoluble substances and test for tin and antimony in the aqueous extract.

Insoluble Substances. The substances of most frequent occurrence which do not yield to the foregoing treatment are:—S, C, AgCl, AgBr, AgI, AgCN, $PbCrO_4$, $PbSO_4$, SnO_2, SnS_2, Sb_2O_4, Fe_2O_3, Fe_3O_4, $Fe_4(Fe=C_6N_6)_3$, $SrSO_4$, $BaSO_4$, Al_2O_3, Cr_2O_3, CaF_2, SiO_2 and many silicates. These substances are usually white with the following exceptions: S and AgI are light yellow; SnS_2, "mosaic gold," is deep yellow; $PbCrO_4$ and Fe_2O_3 are reddish; Cr_2O_3 and sometimes CaF_2 are greenish; $Fe_4(Fe=C_6N_6)_3$ is deep blue, Fe_3O_4 and C black.

These substances require special treatment varying with the nature of the compound. It is of great advantage to obtain some indication as to the composition of the substance before treating with other reagents. Unless sufficient indication has already been obtained, examine the insoluble residue according to the methods of the Preliminary Examination especially as directed under C.

If **sulfur** or **carbon** is detected, it must be removed before continuing the analysis. This may be accomplished most conveniently by ignition. Sulfur will burn to SO_2 which may be recognized by its odor. Carbonaceous matter burns to CO_2, the black substance disappearing entirely or leaving only a slight white ash.

If **silver** is indicated, cover the substance with a piece of metallic zinc and add dilute H_2SO_4. Continue the treatment until only a dark residue remains. The zinc, dissolving in the H_2SO_4, throws out the silver in metallic form, leaving the acid radicle in solution, along with the excess of zinc sulfate, where it may be detected in the usual ways. The silver may be obtained in solution by dissolving the washed residue in nitric acid.

If **lead** is indicated, fuse the substance with 4–5 times its weight of a mixture of Na_2CO_3 and K_2CO_3 on a piece of *sheet iron*—platinum may be ruined—cool, extract with boiling water and test for H_2SO_4 and $H_2Cr_2O_7$. The lead may be obtained in solution by dissolving the washed residue in acetic or nitric acid.

If **tin** or **antimony** is indicated, fuse the substance in a porcelain crucible with its own weight of NaOH and an equal amount of sulfur. This will form soluble thiostannates or thioantimonates (see pages 141 and 169) and in the aqueous extract, treated as Filt. 5, these elements may be detected and confirmed in the regular way.

If **no metal other than iron** is indicated by the preliminary test, fuse the substance in a platinum crucible with 4–5 times its weight of the Na_2CO_3—K_2CO_3 mixture and add a few crystals of KNO_3. Cool, boil out with a little water and test the aqueous extract for the acids possibly present; also for aluminum and chromium which are present (if present at all), the former as

Na_3AlO_3 and the latter as Na_2CrO_4. Dissolve the insoluble residue, after washing, in HCl and test the solution for the bases.

By this fusion, cyanids, either simple or complex, are completely oxidized, hence this acid cannot be detected in the resulting solution. All cyanids are decomposed by heating with dilute H_2SO_4 (1:2) with the liberation of HCN which may be collected in a trap containing NaOH. After washing out the contents of the trap into a test-tube, hydrocyanic acid may be detected in the usual ways. (See page 294.)

Some **silicates** and **ignited oxids** are not decomposed readily by fusion with the $Na_2CO_3 — K_2CO_3$ mixture but yield to the action of fused acid potassium sulfate, $HKSO_4$. The substance, mixed with 4–5 times its bulk of the acid sulfate, may be fused in a test-tube over a Bunsen flame for about one half hour at a temperature just high enough to cause a slight liberation of white fumes of sulfur trioxid. (See page 188.)

Alkalies present in insoluble silicates can not be determined after either of these methods of treatment inasmuch as salts of the alkalies are introduced during the process. Resort is had to the following method. The finely powdered silicate is mixed with an equal amount of NH_4Cl and 5 times as much $CaCO_3$ and heated to bright redness for half an hour or longer (see page 135). The aqueous extract, after precipitation of calcium by $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$, is evaporated to dryness and ignited to remove ammonium salts. The residue is then moistened with HCl and examined for alkalies by the flame tests.

The Prepared Solution. Before beginning the Acid Analysis, bases other than the alkalies must be removed. This may be satisfactorily accomplished by adding to a portion of the original solution Na_2CO_3 until a strong alkaline reaction is produced. A precipitate will fall which is boiled in the solution for fifteen minutes and then filtered off. By this treatment, all bases except arsenic, antimony and the alkalies are removed as carbonates, or their decomposition products, and the acids remain in solution as soluble alkali salts. Any insoluble salts, other than carbonates, which at first might be precipitated in alkaline solutions, are subsequently transposed by the boiling Na_2CO_3 solution (see page 68). Thorough boiling should not be neglected, for, otherwise, some acids may be filtered off and lost in the precipitate. If either arsenic or antimony is detected in the Basic Analysis, before adding Na_2CO_3 a portion of the original solution is made strongly acid with HCl and H_2S is introduced as long as a precipitate falls. To the filtrate from this solution, Na_2CO_3 is added and the treatment finished as directed. The solution thus made ready for the Acid Analysis is known as the *prepared solution*.

It is advantageous and customary to make the Basic Analysis before starting the Acid Analysis, inasmuch as the former is more systematic than the latter and indications of certain of the acids present are frequently obtained during the Basic Analysis. At the beginning of the Acid Analysis, preliminary tests are made indicating the presence or absence of certain groups of acids. Further than this, the Acid Analysis consists, generally, in making individual tests for each acid that has not been excluded by the preliminary tests from the number of those possibly present. A consideration of the solubility of the original substance will exclude certain acids at once. For instance, if the original substance is soluble in water and barium is the metal present, it is unnecessary to make tests for H_2SO_4, H_3PO_4, H_2SiO_3 and others, for the barium salts of these acids are not soluble in water as a glance at the Table of Solubilities (pages 330 and 331) will show. Similarly, if silver has been found in a compound forming a neutral solution with water, the same table indicates that the only acids that can be present are HF, HNO_3, HNO_2, $H(C_2H_3O_2)$, $HClO_3$, $HClO_4$, $HMnO_4$ and H_2SiF_6. By intelligent use of this Table of Solubilities the Acid Analysis may usually be greatly simplified and shortened.

Liquids submitted for qualitative analysis generally consist of aqueous solutions. After noting the reaction of a solution to litmus, the remainder of the preliminary examination may usually be omitted. If the solution is very acid, remove as much of the excess of acid as is possible by evaporating nearly to dryness, after which dilute with water and proceed with the Basic Analysis. If the solution is alkaline, make faintly acid with HNO_3. If a precipitate falls, filter and consider the filtrate as the original solution and analyze for bases and acids. Treat the precipitate (if there is one) according to the methods for insoluble substances.

Gases can be satisfactorily analyzed, usually, only by the methods of Gas Analysis, for which the student is referred to the standard manuals on the subject.

PRELIMINARY EXAMINATION OF SOLIDS.

For these tests small portions of the original substance may be used. If the original substance be in solution, its reaction to litmus should be noted. Otherwise, the preliminary examination may usually be omitted without detriment. If it is desirable to make these tests, small portions of the residue left by evaporation to dryness may be used. Blackening or charring on evaporation to dryness is an indication of the presence of organic matter.

Note carefully the appearance and physical properties of the original substance and draw inferences according to previous experience.

A. Heat in a Closed-tube of Hard Glass. (See pages 53–55.)

Observation.	*Indication.*
1. **Change of color**:	Presence or formation of—
Yellow, hot; straw-color, cold	ZnO.
Yellow-red, hot; yellow, cold; fusible	PbO.
Yellow-brown, hot; dirty white, cold	SnO_2.
Orange, hot; light yellow, cold; fusible	Bi_2O_3.
Dark red, hot; yellow, cold; fusible	$PbCrO_4$, or alkali chromate.
Yellow, easily fusible to brown liquid	S, free or from polysulfids.
Red, cold; black, hot; globules of Hg	HgO.
Dull red, cold; red-black, hot	Fe_2O_3.
Becomes black on heating—	
(*a*) often showing blue or green color previously	Co or Cu salts.
(*b*) chars	Organic matter.

Observation.	*Indication.*
2. **Evolution of volatile matter:**	Presence or formation of—
Brown color, characteristic odor.. N_2O_4.	Nitrate or nitrite.
Violet color, characteristic odor, black sublimate..............I	Iodin, or iodid with oxidizing agent.
Brown-red color, characteristic odor ....Br.	Bromid with an oxidizing agent.
Pale green color, characteristic odor ....Cl.	Chlorid with an oxidizing agent.
Colorless, odor of burning sulfur, acid reaction................SO_2.	Sulfur, sulfid, sulfite, thiocyanate, sulfate with reducing matter or other sulfur compound.
Colorless, characteristic odor....H_2S.	Sulfid, or sulfur compound with reducing matter.
Colorless, making "lime-water" turbid ....CO_2.	Carbonate or organic matter.
Colorless, characteristic odor, alkaline reaction...............NH_3.	Ammonium salt.
Colorless, characteristic odor, burns with pink flame........ $(CN)_2$.	Cyanid or thiocyanate.
Colorless, odor of "burned sugar," inflammable.	Organic matter.
Colorless, kindling glowing spark O.	Chlorate, nitrate, peroxid or unstable oxid.
Condenses to a clear liquid, turning dehydrated $CuSO_4$ blue...H_2O.	Moisture, water of crystallization or water formed during decomposition.
—if acid in reaction..........	Volatile acid or acid salt.
—if alkaline in reaction.......	Ammonium salt.
3. **Formation of a sublimate:**	Presence or formation of—
White	Ammonium salt or some organic substance.
White, crystalline..............Sb_2O_3.	Antimonious oxid.
White, crystalline..............As_2O_3.	Arsenious oxid.
White, crystalline..............$HgCl_2$.	Mercuric chlorid.
White, yellow when hot........ $(HgCl)_2$.	Mercurous chlorid.
Yellow ....As_2S_3.	Arsenious sulfid.
Yellow, red when rubbed.......HgI_2.	Mercuric iodid.
Black ....As.	Arsenic.
Black, violet vapor............I.	Iodin.
Black, red when rubbed.........HgS.	Mercuric sulfid.
Metallic mirror or globules.....Hg.	Mercury.

B. Heat with Concentrated Sulfuric Acid in a Test-tube. (See page 55.)

Observation.	*Indication.*
Evolution of gas:	Presence or formation of—
Brown color, characteristic odor.. N_2O_4.	Nitrate or nitrite.
Violet color, characteristic odor, black deposit .... I.	Iodin or iodid.
Brown-red color, characteristic odor .... Br.	Bromid.
Pale green color, characteristic odor .... Cl.	Hypochlorite, chlorate, or chlorid with an oxidizing agent.
Green-yellow color, characteristic odor, explosive.............. ClO_2.	Chlorate.
Colorless, odor of burning sulfur SO_2.	Sulfite, thiosulfate, or reducing matter, possibly H_2S, acting on the sulfuric acid.
Colorless, odor of burning sulfur accompanied by blackening..	Organic matter.
Colorless, characteristic odor darkens lead-acetate paper.... H_2S.	Sulfid.
Colorless, making "lime-water" turbid .... CO_2.	Carbonate or oxalate.
Colorless, odor of bitter almonds HCN.	Cyanid.
Colorless, characteristic odor, acid reaction .... $H(C_2H_3O_2)$.	Acetate.
Colorless, characteristic odor, acid reaction .... HCl.	Chlorid.
Colorless, characteristic odor, acid reaction, etches glass......... HF.	Fluorid.
Colorless, deposits silicic acid on contact with water .... SiF_4.	Silicofluorid, or fluorid with silicate or silicic anhydrid.
Colorless, burning with blue flame .... CO.	Cyanid or oxalate.

C. Heat on Charcoal. (See page 55.)

(*a*) *Without other reagents.*

Observation.	*Indication.*
1. **The substance fuses and is absorbed by the charcoal.**	Salts of Li, Na or K.
2. **The substance is infusible:**	
Moistened with water gives alkaline reaction.	BaO, SrO, CaO or MgO.
Moistened with dilute solution of cobalt nitrate and reheated turns ....Blue.*	Al_2O_3.
Green.	ZnO.
3. **The substance deflagrates.........**	Nitrates or chlorates.
4. **A coating forms on the charcoal:**†	
White, garlic odor.............As_2O_3.	Arsenic.
White, near the residue........Sb_2O_3.	Antimony.
Yellow, hot; white, cold........ZnO.	Zinc.
Yellow-red, hot; yellow, cold...PbO.	Lead.
Yellow-brown, hot; dirty white, cold, very near residue.......SnO_2.	Tin.
Orange, hot; light yellow, cold...Bi_2O_3.	Bismuth.
Brown-orange, hot; same, cold...CdO.	Cadmium.

(*b*) *With Na_2CO_3 and powdered charcoal.*

1. **Metallic globule is formed:**‡

Without coating on charcoal—	yellow,	Gold.
	red,	Copper.
	white, malleable,	Silver.

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* Some silicates give a pale blue color on similar treatment.

† The indications given by the oxids here formed as coatings on the charcoal may be obtained by what is known as the **film test.** A small portion of the substance (dry or in solution) is heated on a few fibres of asbestos in the oxidizing flame of a Bunsen burner so placed under a porcelain dish containing cold water that any volatile matter will be condensed upon it. On exposure of the sometimes invisible film to H_2S the characteristic color of the corresponding sulfid will be developed.

Film.	*With H_2S.*	*Indication.*
White.	White.	Zinc.
White.	Yellow.	Arsenic.
White.	Orange.	Antimony.
White.	Yellow or brown.	Tin.
Yellow (pale).	Brown.	Bismuth.
Yellow.	Black.	Lead.
Brown.	Yellow.	Cadmium.

‡ These metallic globules may be very satisfactorily obtained by what is known as the **match test.** On a crucible cover fuse a piece of crystallized sodium carbonate

With coating on charcoal as in *C*(*a*)4—	white, malleable,	Tin or lead* (see pages 138 and 142).
	white, brittle,	Antimony or Bismuth (see pages 165 and 170).
2. **Magnetic mass is formed:**	dark, brittle,	Iron, cobalt or nickel.

D. Heat in a Borax-bead. (See page 56.)

The bead is colored:

In oxidizing flame —	In reducing flame—	
Blue.	Blue.	Cobalt.
Blue.	Red, opaque.	Copper.
Green.	Green.	Chromium.
Yellow.	Green.	Iron.
Brown.	Gray, opaque.	Nickel.
Amethyst.	Nearly colorless.	Mangaese.

E. Heat on Platinum Wire in Bunsen Flame. (See page 56.)

The flame is colored:	Yellow.	Sodium.
	Lavender.	Potassium.
	Orange.	Calcium.
	Crimson.	Strontium.
	Carmine.	Lithium.
	Green.	Copper or boric acid.
	Green, yellowish.	Barium.
	Blue, brilliant.	Cupric chlorid.
	Blue, pale.	Arsenic.

$Na_2CO_3.10H_2O$, and rub a match from which the tip has been removed in the solution thus formed until the wood is saturated. Char the match in a Bunsen burner, dip it in the finely powdered substance and heat again in the reducing flame when the metallic globule will appear.

* In these as in other cases where it is necessary to determine the composition of very small amounts of matter, a whole series of reactions may be performed by placing the substance in solution and making separate tests on single drops transferred by means of a glass rod to a porcelain surface or filter paper. By means of the glass rod single drops of reagents (NaOH, Na_2CO_3, $(NH_4)_2S$, NH_4OH, HCl, H_2SO_4, K_2CrO_4, KI, KCN, $K_4(Fe=C_6N_6)$, $K_3(Fe\equiv C_6N_6$, KSCN—some of these or others as suggested by the results obtained) may be added and the character of typical compounds of the metallic component noted. The formation of white compounds is best detected by placing the drops on a dark surface. This together with the film test and match test are some of the methods of **microchemical analysis.**

THE BASIC ANALYSIS.

Group Separations.—The following scheme indicates the manner in which the base-forming elements are divided into groups, the members of which are individually separated and identified subsequently. In the solution to be analyzed, certain of the following list of kathions are present. Any changes caused by the addition of reagents, such as the removal of certain ions by precipitation in the form of insoluble salts, are indicated by the scheme.

$\overset{+}{\mathrm{Ag}}$, $(\overset{+}{\mathrm{Hg}})_2$, $\overset{++}{\mathrm{Pb}}$, $\overset{++}{\mathrm{Hg}}$, $\overset{+++}{\mathrm{Bi}}$, $\overset{++}{\mathrm{Cu}}$, $\overset{++}{\mathrm{Cd}}$, $\overset{+++}{\mathrm{As}}$, $\overset{+++++}{\mathrm{As}}$, $\overset{+++}{\mathrm{Sb}}$, $\overset{+++++}{\mathrm{Sb}}$, $\overset{++}{\mathrm{Sn}}$, $\overset{++++}{\mathrm{Sn}}$, $\overset{+++}{\mathrm{Al}}$, $\overset{+++}{\mathrm{Cr}}$, $\overset{+++}{\mathrm{Fe}}$, $\overset{++}{\mathrm{Fe}}$, $\overset{++}{\mathrm{Co}}$, $\overset{++}{\mathrm{Ni}}$, $\overset{++}{\mathrm{Mn}}$, $\overset{++}{\mathrm{Zn}}$, $\overset{++}{\mathrm{Ba}}$, $\overset{++}{\mathrm{Sr}}$, $\overset{++}{\mathrm{Ca}}$, $\overset{++}{\mathrm{Mg}}$, $\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$.

HCl, *i. e.*, $\overset{-}{\mathrm{Cl}}$, forms *Group I, Div. A.* **AgCl, $\mathbf{(HgCl)_2}$, $\mathbf{PbCl_2}$.**	$\overset{++}{\mathrm{Pb}}$, $\overset{++}{\mathrm{Hg}}$, $\overset{+++}{\mathrm{Bi}}$, $\overset{++}{\mathrm{Cu}}$, $\overset{++}{\mathrm{Cd}}$, $\overset{+++}{\mathrm{As}}$, $\overset{+++++}{\mathrm{As}}$, $\overset{+++}{\mathrm{Sb}}$, $\overset{+++++}{\mathrm{Sb}}$, $\overset{++}{\mathrm{Sn}}$, $\overset{++++}{\mathrm{Sn}}$, $\overset{+++}{\mathrm{Al}}$, $\overset{+++}{\mathrm{Cr}}$, $\overset{+++}{\mathrm{Fe}}$, $\overset{++}{\mathrm{Fe}}$, $\overset{++}{\mathrm{Co}}$, $\overset{++}{\mathrm{Ni}}$, $\overset{++}{\mathrm{Mn}}$, $\overset{++}{\mathrm{Zn}}$, $\overset{++}{\mathrm{Ba}}$, $\overset{++}{\mathrm{Sr}}$, $\overset{++}{\mathrm{Ca}}$, $\overset{++}{\mathrm{Mg}}$, $\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$.
H_2S, *i. e.*, $\overset{=}{\mathrm{S}}$, forms *Group I, Divs. A and B.* **PbS, HgS, $\mathbf{Bi_2S_3}$, CuS, CdS, $\mathbf{As_2S_3}$, $\mathbf{As_2S_5}$, $\mathbf{Sb_2S_3}$, $\mathbf{Sb_2S_5}$, SnS, $\mathbf{SnS_2}$.** $(NH_4)_2S.xS$ gives a— Res.—*Group I, Div. B.* **PbS, HgS, $\mathbf{Bi_2S_3}$, CuS, CdS.** Filt.—*Group I, Div. C.* $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ $(NH_4)_2SnS_3$. HCl, *i. e.*, $\overset{+}{\mathrm{H}}$, forms *Group I, Div. C.* **$\mathbf{As_2S_5}$, $\mathbf{Sb_2S_5}$, $\mathbf{SnS_2}$.**	$\overset{+++}{\mathrm{Al}}$, $\overset{+++}{\mathrm{Cr}}$, $\overset{++}{\mathrm{Fe}}$, $\overset{++}{\mathrm{Co}}$, $\overset{++}{\mathrm{Ni}}$, $\overset{++}{\mathrm{Mn}}$, $\overset{++}{\mathrm{Zn}}$, $\overset{++}{\mathrm{Ba}}$, $\overset{++}{\mathrm{Sr}}$, $\overset{++}{\mathrm{Ca}}$, $\overset{++}{\mathrm{Mg}}$, $\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$. Boil with HNO_3. $\overset{+++}{\mathrm{Al}}$, $\overset{+++}{\mathrm{Cr}}$, $\overset{+++}{\mathrm{Fe}}$, $\overset{++}{\mathrm{Co}}$, $\overset{++}{\mathrm{Ni}}$, $\overset{++}{\mathrm{Mn}}$, $\overset{++}{\mathrm{Zn}}$, $\overset{++}{\mathrm{Ba}}$, $\overset{++}{\mathrm{Sr}}$, $\overset{++}{\mathrm{Ca}}$, $\overset{++}{\mathrm{Mg}}$, $\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$.
$NH_4(C_2H_3O_2)$ and boiling forms *Group II.* **$\mathbf{Al(OH)_2(C_2H_3O_2)}$, $\mathbf{Cr(OH)_2(C_2H_3O_2)}$, $\mathbf{Fe(OH)_2(C_2H_3O_2)}$.**	$\overset{++}{\mathrm{Co}}$, $\overset{++}{\mathrm{Ni}}$, $\overset{++}{\mathrm{Mn}}$, $\overset{++}{\mathrm{Zn}}$, $\overset{++}{\mathrm{Ba}}$, $\overset{++}{\mathrm{Sr}}$, $\overset{++}{\mathrm{Ca}}$, $\overset{++}{\mathrm{Mg}}$, $\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$.
$(NH_4)_2S$, *i. e.*, $\overset{=}{\mathrm{S}}$, forms *Group III.* **CoS, NiS, MnS, ZnS.**	$\overset{++}{\mathrm{Ba}}$, $\overset{++}{\mathrm{Sr}}$, $\overset{++}{\mathrm{Ca}}$, $\overset{++}{\mathrm{Mg}}$, $\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$.
$(NH_4)_2CO_3$, *i. e.*, $\overset{=}{\mathrm{CO_3}}$, forms *Group IV.* **$\mathbf{BaCO_3}$, $\mathbf{SrCO_3}$, $\mathbf{CaCO_3}$.**	$\overset{++}{\mathrm{Mg}}$, $\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$.
HNa_2PO_4, *i. e.*, $\overset{-}{\mathrm{PO_4}}$, precipitates (one metal only of) *Group V.* **$\mathbf{Mg(NH_4)PO_4}$.**	$\overset{+}{\mathrm{Li}}$, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $(\overset{+}{\mathrm{NH_4}})$.

SPECIAL TESTS.

Certain base-forming substances, such as ammonium and iron, are introduced as reagents into the solution to be investigated during the course of the analysis. Others, originally present in one condition, are likely to be changed, *i. e.,* oxidized or reduced, during the process. It is necessary, therefore, to test for the presence and condition of certain substances before beginning the systematic Basic Analysis.

Test for Ammonium, (NH_4).

Heat a small portion of the original dry substance with dry $Ca(OH)_2$, or add to a small portion of the *original solution* NaOH or KOH until the solution is strongly alkaline and boil. The liberation of pungent fumes of ammonia, NH_3, which turn moist red litmus-paper blue, indicates $\mathbf{(NH_4)}$. (See page 76.)

Test for the Presence and Condition of Iron, Fe.

(1) Acidify a small portion of the *original solution* with HCl and add a drop of $K_4(Fe=C_6N_6)$.

Dark blue prec., $\mathbf{Fe_4(Fe=C_6N_6)_3}$, indicates **Fe**, present in the trivalent or *ferric* condition.

(2) Acidify a small portion of the *original solution* with HCl and add a drop of $K_3(Fe\equiv C_6N_6)$ solution, freshly prepared by dissolving a small crystal in water. Dark blue prec., $\mathbf{Fe_3(Fe\equiv C_6N_6)_2}$, indicates **Fe**, present in the bivalent or *ferrous* condition. (See page 227.)

Test to Determine the Condition of Tin, Sn.

Acidify a small portion of the *original solution* with HCl, filter, if necessary to obtain a clear solution and add a few drops of $HgCl_2$. (See page 110.)

White prec., $\mathbf{(HgCl)_4}$, which may turn dark on standing, **Hg**, indicates **Sn**, present in the bivalent or *stannous* condition.

If tin is found during the Basic Analysis and no prec. is obtained here, it must be present in the tetravalent or *stannic* condition.

SEPARATION AND ANALYSIS OF GROUP I, DIV. A.

(If HCl was used in making the solution (see page 239), proceed at once to the Separation of Group I, Divs. B and C, page 252.)

To the *original solution* add *one-tenth* its volume of conc. HCl. **Shake thoroughly, filter, and wash the prec. with cold water.**

Prec. 1. *Group I, Div. A.*
AgCl, $(HgCl)_2$, $PbCl_2$.

Filt. 1. ***Group I, Divs. B and C and Groups II–V.*** See page 252.

Treat on the filter paper thoroughly with boiling water and allow the washings to filter through into a test-tube or beaker.

Res. 2. AgCl, $(HgCl)_2$,

Wash thoroughly with boiling water until the washings no longer give a test for lead.

Reject the washings.

Moisten thoroughly with 2–3 ccm. NH_4OH, avoiding any excess of the reagent, and wash with a little water.

Res. 3. Hg_2NH_2Cl.

Black coloration indicates **Hg**.

Treat on the filter paper with a little warm aqua regia and wash into a test-tube. (Filter if necessary to remove any AgCl or filter fibre.) To the clear filt. add $SnCl_2$. White prec., **$(HgCl)_2$**, or dark, **Hg**, confirms **Hg**.

Filt. 3.

Acidify with HNO_3. White prec., **AgCl**, darkening in sunlight, indicates *Ag*.[*]

Filt. 2.

Divide into three portions.

A. Add 2 or 3 drops K_2CrO_4. Yellow prec., $PbCrO_4$, soluble in NaOH, indicates Pb.

B. Add H_2SO_4 and allow to stand for a few minutes if necessary. White prec., $PbSO_4$, soluble in NaOH, indicates Pb.

C. Add KI.[†] Yellow spangles, **PbI_2**, soluble in hot water, recrystallizing on cooling, indicate **Pb**.

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[*] If no indication of the presence of Ag is obtained here and a blackening indicating mercury was noted in the proper place, it is safest to test the Hg prec. for Ag also. After treatment with aqua regia, any Ag present will be in the form of the chlorid which may be filtered off (see treatment of Res. 3) and its solubility tested in NH_4OH, KCN or $Na_2S_2O_3$.

[†] A few drops only, as an excess, will form the soluble double salt, K_2PbI_4 (see page 145).

DISCUSSION OF THE SEPARATION AND ANALYSIS OF GROUP I, DIV. A.

The separation of Group I, Div. A from the salts of other metals which may be present in solution depends on the relative insolubility of the chlorids of these elements and the solubility of other chlorids. The separation is not exact, however, since $PbCl_2$ is very appreciably soluble and will not be precipitated at all from solutions containing one per cent. or less of the Pb salt. For this reason Pb, if present, will always be found in Group I, Div. B but may not be detected in Div. A. On the other hand, the oxychlorids of Sb and Bi ($SbOCl$ and $BiOCl$) are quite insoluble and may be precipitated by a small amount of HCl. These salts will dissolve in an excess of acid, however, hence the reason for adding conc. HCl to the extent of one-tenth the volume of the solution.

Mercury as well as Pb may be found in both Divs. A and B of Group I. The chlorid formed by the mercuric ion, $\overset{++}{Hg}$, is soluble, hence salts of mercury in the divalent condition are separated from the univalent mercurous compounds, for the chlorid formed by the mercurous ion, $(\overset{+}{Hg})_2$, is highly insoluble.

The solubility of $PbCl_2$ in boiling water offers an easy means of separation from Ag and Hg in the lower condition, the chlorids of these metals being practically insoluble. Under certain conditions, the prec. of $(HgCl)_2$ is so finely divided as to wash through the filter paper to some extent and give a cloudy filt. If Pb is absent, or present in small amount only, a reddish coloration due to Hg_2CrO_4 may appear on adding the CrO_4 ion. Since the Hg salt is insoluble in NaOH or KOH, it may be distinguished from the Pb salt which dissolves readily with the formation of an alkaline plumbite solution containing the ion $\overset{--}{PbO_2}$. (See page 144.)

The formation of complex ions on treatment with NH_4OH is the basis of the separation of Hg and Ag, since the compounds formed by the ion $\overset{+}{Ag(NH_3)_2}$ are soluble while compounds formed by $(Hg)_2NH_2$ are insoluble. Salts of this latter type decompose immediately into metallic Hg and compounds containing the radicle $\left(—Hg—N<^{H}_{H}\right)$. Since the $\overset{+}{Ag}$ ion, and more readily the $\overset{+}{Ag(NH_3)_2}$ ion, is reduced to the metal by Hg, in the presence of a large amount of the Hg salt a small amount of Ag salt may be entirely decomposed in this way and remain as metallic Ag in the black residue. A large excess of NH_4OH is to be avoided, therefore. The mercury compound may be decomposed and the metal driven off by igniting in porcelain under a hood, after which the Ag may be dissolved in HNO_3 and tested for in the usual way. Or, the black residue may be dissolved in aqua regia, by the action of which all Hg, both free and combined, is oxidized to $HgCl_2$. This may be separated from the insoluble AgCl by filtration (see foot-note on opposite page). Stannous chlorid, $SnCl_2$, being a strong reducing agent, reduces $HgCl_2$ first to white $(HgCl)_2$ and finally to Hg which in finely divided condition is black.

Should Filt. 3 be milky, it is probably due to the fact that all $PbCl_2$ was not washed out of Res. 2. With NH_4OH, $PbCl_2$ forms a basic chlorid which is very apt to run through the filter. It will dissolve in HNO_3, however, hence will not interfere with the test for Ag.

SEPARATION OF GROUP I, DIVS. B AND C.

Dilute Filt. 1 with an equal volume of water, warm and pass H_2S until precipitation ceases. Filter and test a portion of the filt. by diluting with three volumes of water and again passing H_2S. Should precipitation occur again, dilute the whole filt. and pass H_2S again until precipitation is complete. Filter and wash with hot water.

Prec. 4. *Group I, Divs. B and C.*
HgS, PbS, Bi_2S_3, CuS, CdS, Sb_2S_3, Sb_2S_5, As_2S_3, As_2S_5, SnS, SnS_2 (Au_2S_3, PtS_2).
Puncture the filter paper and wash the prec. into a test-tube or small beaker with 5–10 ccm. of yellow ammonium sulfid, $(NH_4)_2S.xS$. Warm, filter and wash.

Filt. 4. *Groups II–V.*
Boil out H_2S* immediately and treat as directed on page 260.

Res. 5. *Group I. Div. B.*
Analyze as directed on page 254.

Filt. 5. *Group I, Div. C.*
Acidify with HCl and filter.

Prec. 6. *Group I, Div. C.*
As_2S_5, Sb_2S_5, SnS_2, S, (Au_2S_3, PtS_2).
Analyze as directed on page 256.

Filt. 6. Reject.

DISCUSSION OF THE SEPARATION OF GROUP I, DIVS. B AND C.

The separation of Group I from the other groups of metals which may be present in solution depends on the fact that the sulfids of Ag, Hg, Pb, Bi, Cu, Cd, As, Sb and Sn are relatively insoluble in water and dilute acid. The sulfids of Group II and of Mg are hydrolyzed completely in aqueous solution with the precipitation of hydroxids insoluble in water but soluble in dilute acid. The sulfids of Group III are either soluble in dilute acid or their precipitation is prevented by it. The sulfids of Group IV and V are soluble. Hence, in the presence of dilute acid, only the sulfids of Group I are precipitated.

The metals of Group I, Div. A are not ordinarily precipitated as sulfids, however. Because of the relative insolubility of the chlorids of Ag, Hg(ous), and Pb, Div. A is separated after the addition of HCl and before the addition of the sulfid ion. Consequently Divs. B and C only are ordinarily precipitated as sulfids.

Since H_2S is a reducing agent, if oxidizing agents be present in solution, an interaction will take place resulting in the oxidation of H_2S to H_2O and S, or to H_2SO_4. Under these circumstances sulfids are precipitated only after all oxidizing agents have been reduced. If present in considerable amounts, the products of this reaction, mostly S, may lead to difficulties and cause confusion in the analysis of the precipitate.

Hence it is better to remove any oxidizing agent before beginning the analysis as directed on page 239. If present in small amounts only, they will not interfere but may give an indication of some of the elements present. A pink or purple solution of a permanganate is bleached as the H_2S enters. An orange chromate solution is turned green and S is precipitated. However, if Pb is present in small amounts only, the formation of $PbSO_4$ from the oxidation of H_2S may cause some difficulty. In this case, Res. 7 should be tested for Pb as well as Hg.

---

* The point at which H_2S has been entirely removed is indicated by the fact that a filter paper, moistened with $Pb(C_2H_3O_2)_2$ and held in the vapor from the solution, is no longer blackened.

The sulfids of Div. C, especially the As sulfids, may be most satisfactorily precipitated in the presence of considerable acid. This prevents the formation of soluble salts of the thioacids and of colloidal precipitates at the same time. Hence it is better not to dilute Filt. 1 too extensively before passing H_2S. On the other hand, PbS is soluble in fairly strong HCl and CdS in a concentration greater than 4 per cent. The precipitation is made in a hot solution to hasten the reactions and prevent colloidal precipitates which sulfids as a class show strong tendency to form. The final dilution and testing of the filtrate as directed is essential to insure the precipitation of CdS which, if not removed here, will come down with Group III. Thorough washing of Prec. 4 is necessary to remove members of other groups, as otherwise Al or Fe may interfere with the test for Bi as indicated in foot-note on page 254.

It is absolutely necessary that Filt. 4 be boiled free from H_2S immediately, for otherwise, the oxygen of the air will convert it into H_2SO_4 and cause the precipitation of sulfates of Group IV (Res. 21).

The separation of Divs. B and C from each other depends on the solubility of the sulfids of Div. C in alkaline polysulfids and the relative insolubility of the sulfids of Div. B. Ammonium polysulfid, $(NH_4)_2S.xS$, gives the sharpest separation but even this is not exact, for if a large excess of the reagent is used, CuS may be dissolved in part and pass into the filtrate to interfere with the test for Sb. (See foot-note, page 256.)

Colorless alkaline sulfids of the type, $(NH_4)_2S$ dissolve As_2S_5, Sb_2S_5 and SnS_2 to form soluble thioarsenates, thioantimonates and thiostannates (see pages 164, 169, 141) and As_2S_3 and Sb_2S_3 will dissolve in the same reagent, forming soluble thioarsenites and thioantimonites. Stannous sulfid, SnS, does not form a corresponding thiostannite, however, and will not dissolve in colorless $(NH_4)_2S$. For this reason it is necessary to use the yellow polysulfid, $(NH_4)_2S.xS$. The additional S in compounds of this type oxidizes SnS to SnS_2, which then dissolves to form the thiostannate. At the same time, the sulfids of any trivalent As or Sb present are oxidized to the pentavalent condition, thus furnishing an example of the oxidizing action of S.

Whether any of these thioacids are capable of existence in the free state is very questionable. At any rate they decompose immediately into H_2S and the metallic sulfid (for reactions see page 165). Consequently on acidifying a solution of their salts, As_2S_5, Sb_2S_5 and SnS_2 are precipitated. Even if present originally in the lower condition, after oxidation by the polysulfid, only the higher sulfids are precipitated on acidifying.

Inasmuch as all polysulfids separate free S when treated with acids (see page 184), some precipitate is always obtained in this place whether Div. C be present or not. The sulfids of these elements are deep yellow or orange in color and are flocculent in character, while the precipitated S is usually straw-colored, very finely divided and does not tend to gather together to any great extent, giving rather a milky solution which passes through a filter.

ANALYSIS OF GROUP I, DIV. B.

Res. 5. From page 252. *Group I, Div. B.* **HgS, PbS, Bi_2S_3, CuS, CdS.** Puncture the filter paper and wash the res. into a test-tube with 5–10 ccm. water. Add *one-half* its volume of conc. HNO_3 and boil for two or three minutes. Dilute with an equal volume of water and filter.

Res. 7. Black **HgS** or white **$HgS.Hg(NO_3)_2$** or possibly **$PbSO_4$**.

Dissolve in a *small amount* of aqua regia, dilute, boil to remove chlorin and filter. To the filt. add $SnCl_2$. White prec., **$(HgCl)_2$**, or dark, **Hg**, indicates the presence of **Hg**.

Filt. 7. Add a few drops of conc. H_2SO_4 and evaporate until dense white fumes of SO_3 appear. Cool, dilute, and, if the solution is not distinctly acid, add 2–3 ccm. H_2SO_4 and filter.

Res. 8. White **$PbSO_4$**.

Confirm by dissolving in a few drops of NaOH. Add K_2CrO_4 and acidify faintly with $H(C_2H_3O_2)$. Yellow prec., **$PbCrO_4$**, indicates **Pb**.

Filt 8. Add NH_4OH until solution is alkaline and filter.

Prec. 9. White* **$Bi(OH)_3$**.

Add a few drops of *dil.* HCl to the prec. on the paper and allow to filter through into a beaker of water.

White prec. **BiOCl** indicates **Bi**.

Or, wash prec. on the filter and add a few drops of Na_2SnO_2.†

Dark coloration, **BiO**, indicates **Bi**.

Filt. 9. Blue solution indicates **Cu**. *If Cu is indicated,* test for Cd as in B (1).

If no color appears, divide filt. Test one portion for Cu as in A, and another for Cd as in B (1) or B (2) according as Cu is or is not indicated in A.

A. Acidify with $H(C_2H_3O_2)$ and add $K_4(Fe{=}C_6N_6)$. Mahogany-colored prec., **$Cu_2(Fe{=}C_6N_6)$** indicates **Cu**.

B (1). If Cu is indicated, add KCN somewhat in excess of the amount necessary to cause the blue color to disappear. Pass H_2S.

Yellow prec.,‡ **CdS**, indicates **Cd**.

(2) If Cu is not indicated, acidify *slightly* with HCl and pass H_2S.

Yellow prec., **CdS**, indicates **Cd**.

---

* Sometimes slightly colored brown by traces of $Fe(OH)_3$ if Prec. 4 is not thoroughly washed. For the same reason a slight white prec. which will not give confirmatory tests for Bi may be $Al(OH)_3$.

† Sodium stannite (Na_2SnO_2) solutions must be freshly prepared each time just previously to using. A few drops of $SnCl_2$ solution are treated with NaOH or KOH with vigorous shaking until the prec. first formed *just redissolves*, thus avoiding any excess of alkali. (See page 139.)

‡ If a dark prec. falls, it is due to traces of Pb or Hg and possibly Bi but is not due to Cu if sufficient KCN has been added. Filter off the prec., puncture the paper and wash into a test-tube with 10 ccm. water. Add 2 ccm. conc. H_2SO_4, boil and filter. Dilute the filt. with an equal volume of water and pass H_2S, neutralizing part of the acid present with NH_4OH if necessary to bring down a prec. Yellow prec., **CdS**, indicates **Cd**.

DISCUSSION OF THE ANALYSIS OF GROUP I, DIV. B.

Although the sulfids of Div. B are not caused to pass into solution by the presence of the $\overset{+}{H}$ ion, with the exception of HgS they do dissolve in dilute HNO_3 because of its oxidizing action. The separation of Hg from the other members of this Div. depends upon this fact, yet it may sometimes be not altogether exact. Some of the complex Hg salts, at first precipitated by H_2S from acid solutions (see page 108), are soluble in HNO_3 and, if not entirely changed into the simple HgS, will cause Hg to pass into Filt. 7 to form a black precipitate later and interfere with the test for Cd. Treatment with $(NH_4)_2S \cdot x\,S$ insures complete transformation of these intermediate Hg compounds into HgS. If, for any reason, the regular separation of Divs. B and C by means of this reagent is omitted, it is advisable to moisten the precipitated sulfids with a little diluted $(NH_4)_2S\,x\,S$.

The oxidation of these sulfids by means of HNO_3 results, for the most part, in free S but some H_2SO_4 may be formed, especially if the acid be stronger than 5N (i. e. 1 ccm. conc. HNO_3 to 2 ccm. H_2O), or if the boiling be prolonged. Either cause may precipitate some $PbSO_4$ which may remain with the HgS residue.

The separation of Pb depends on the fact that its sulfate is the only one of this Div. relatively insoluble. Inasmuch as $PbSO_4$ dissolves very appreciably in HNO_3, it is necessary to remove the latter to get even an approximate separation. The B. P. of conc. HNO_3 is 120°; the fuming point of H_2SO_4 about 250°. It is fairly certain, therefore, that all HNO_3 will have been removed when the solution has been heated until dense fumes of SO_3 appear. Even after this treatment, however, traces of Pb may be found in Filt. 8 which may darken the precipitate of CdS later in the analysis.

The separation of Bi from Cu and Cd depends upon the fact that in the presence of NH_4OH, $Bi(OH)_3$ is precipitated whereas Cu and Cd form complex ammonia ions, the compounds of which are soluble. The insoluble $Bi(OH)_3$ is transformed by HCl into soluble $BiCl_3$ which, on being largely diluted, partially hydrolyzes and precipitates BiOCl as a faint white cloud. More than a very few drops of HCl must be avoided, since the presence of even a small concentration of $\overset{+}{H}$ ions prevents the formation of this precipitate. For the discussion of the confirmatory test for Bi, see page 171.

The separation of Cu from Cd depends upon the relative stability of the complex cyanid ions, the formation of which is indicated by the bleaching out of the blue color due to the ion $\overset{++}{Cu(NH_3)_4}$. The $(Cu\overline{C_4N_4})$ ion is very stable while the CdC_4N_4 ion is decomposed by H_2S with the precipitation of CdS. For further discussion of this separation, see pages 81 and 84.

Very minute traces of black sulfids other than Cu may darken the CdS precipitate so as to leave the test indefinite. Since, however, CdS is the only sulfid of this Div. soluble in boiling 6N H_2SO_4 (*i. e.*, 1 ccm. conc. H_2SO_4 to 5 ccm. H_2O), a thoroughly satisfactory separation may be effected by this reagent. From the filtrate pure yellow CdS may be precipitated by passing H_2S and neutralizing part of the acid with a few drops of NH_4OH.

Copper present in amounts too small to give a satisfactory blue color with NH_4OH may frequently be detected by means of the ferrocyanid ion, $(Fe = \overline{\overline{C_6N_6}})$, which, with the $\overset{++}{Cu}$ ion, gives a reddish precipitate of great intensity of color. If Cd be present, white $Cd_2(Fe = C_6N_6)$ will be precipitated which may dilute the color given by traces only of Cu so that the precipitate appears flesh-colored.

[illegible]

milky stain in tt - not from C.

ANALYSIS OF GROUP I, DIV. C.

Prec. 6. From page 252. *Group I, Div. C.* **As_2S_5, Sb_2S_5, SnS_2(Au_2S_3, PtS_2).** Puncture the filter and wash the prec. into a test-tube with about 10 ccm. conc. HCl, dilute with ***half its volume*** of water, boil until H_2S is entirely removed and filter.

Res. 10. **As_2S_5 (Au_2S_3, PtS_2).**

A. *If the res. is yellow, i. e., contains no Au or Pt.* Wash the prec. on the filter until the washings give no test for the Cl ion.* Puncture the filter and wash the prec. into a test-tube with 5–10 ccm. HNO_3 and boil thoroughly, evaporating nearly to dryness at least twice, replacing the liquid evaporated by HNO_3. Boil out the res. from the last evaporation with 5–10 ccm. water. Add **$AgNO_3$** and shake thoroughly. Carefully add to the test-tube 2–3 ccm. NH_4OH without shaking.

Formation of a chocolate prec., **Ag_3AsO_4**, in the neutral ring between the acid and alkaline solutions indicates **As.**

B. *If Res. 10 is dark, i. e., probably contains Au or Pt,* proceed as directed on page 258.

Filt. 10. Divide into two portions.

A. Make a little galvanic couple by bringing into contact a piece of platinum and another of zinc.† Immerse the metals in one portion of Filt. 10 to which an equal volume of conc. HCl has been added.

Black deposit;‡ metallic **Sb**, on the platinum electrode indicates **Sb.**

B. To the second portion add 3 or 4 iron nails (not tinned) and allow the action to go on for 10 to 15 minutes or until the solution is colorless, keeping up a steady evolution of hydrogen by the addition of conc. HCl if necessary. Filter the solution into a test-tube containing a clear solution of $HgCl_2$.

White prec., **$(HgCl)_2$**, or dark [illegible]. **Hg**, indicates **Sn.**

---

* Acidify 5 ccm. of the washings with HNO_3 and add a drop of $AgNO_3$. White prec. or cloudiness, **AgCl**, indicates the **Cl** ion.

† The most satisfactory results may be obtained by keeping the contact of the metals outside of the solution to be tested. This may be readily accomplished by bending a strip of Zn into the form shown in Fig. 1. By placing the solution to be

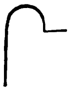

Fig. 1.

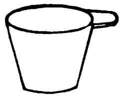

Fig. 2.

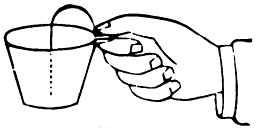

Fig. 3.

tested in a platinum crucible cover or small crucible made with a projecting edge for holding with pincers (Fig. 2), the contact may be easily made as shown in Fig. 3. The Sb is deposited on the inside of the Pt crucible which thus becomes the negative electrode.

‡ Although a heavy black deposit on the platinum always indicates *Sb*, a light stain may be due to Cu if this element is present in the original solution. CuS is somewhat soluble in large amounts of yellow ammonium sulfid and, if dissolved, will appear on the platinum at this point.

If the stain is light and Cu is known to be present in the original solution, dissolve the stain by warming with a few drops of HNO_3 and make the solution alkaline with NH_4OH. If a blue color does not develop, the stain indicates a small amount of Sb present. If a blue color does appear, make faintly acid with HCl and pass H_2S. Treat the precipitated sulfids with Na_2S, filter and acidify with HCl. Orange prec., **Sb_2S_5**, indicates **Sb**.

DISCUSSION OF THE ANALYSIS OF GROUP I, DIV. C.

The separation of As (and of Au and Pt, if present), from the other members of this Div. depends on the insolubility of the sulfids of these elements in HCl and the solubility of Sb_2S_5 and SnS_2. The acid must be fairly strong in order to remove completely Sb and Sn, yet, since boiling is necessary to remove H_2S, long treatment with conc. HCl is likely to dissolve a portion of the As, also. The strength prescribed, about 8 N HCl, should be carefully followed, therefore, in order to obtain satisfactory results.

The separation of Sb from Sn depends upon the different action of HCl upon the two metals. By bringing into contact Pt and Zn and placing them in a solution of a salt, a difference of potential results and an electric current is said to flow. Any metallic ions in solution travel in the direction of the positive electricity and will be deposited on the Pt giving up their charges and passing into the metallic condition. Antimony is only slowly attacked by hot conc. HCl while tin is readily acted upon. Hence Sn dissolves as rapidly as it is deposited and Sb alone remains. If, however, the concentration of the acid falls, Sn may be deposited as a gray crystalline mass either on the Pt because of the electric current or on the Zn because of the greater tendency of this metal to pass into the ionic condition. The smooth black deposit of Sb is not likely to be confused with the gray crystals of Sn. The latter will dissolve in a few moments on adding conc. HCl, leaving the Sb indication. A slight stain of Sb, if moist and exposed to the air, may disappear in a short time owing to oxidation.

In another portion of Filt. 10, Sn may be detected by reducing it to the stannous condition. The color of the solution offers some indication of the progress of the reaction. A yellow color is due to ferric salts; ferrous salts are nearly colorless. Since stannic salts are somewhat more difficult to reduce than ferric salts, it follows that the reduction is not complete as long as the solution shows any yellow color. Aside from stannous salts, no substances able to reduce mercuric chlorid to the lower chlorid or to the metal will be present in this solution. Stannous chlorid has already been used as a reagent for detecting the presence of mercury. Mercuric chlorid is now used as a reagent for stannous salts and, if a reduction takes place on adding $HgCl_2$, it indicates the presence of Sn.

Both PtS_2 and Au_2S_3 are almost black in color, hence if Res. 10 is not dark, neither Pt nor Au can be present. It is only necessary in this case to oxidize As_2S_3 to H_3AsO_4 (see page 50). Arsenic compounds in general are easily oxidized but the S which is always present in excess from the decomposition of the polysulfid renders the oxidation in this case somewhat more difficult by mechanically protecting the As from the action of the acid. Hence it is necessary to evaporate to dryness once or twice to insure oxidation. With the $\overset{+}{Ag}$ ion the $\overset{\equiv}{AsO_4}$ ion produces a chocolate-colored precipitate which is extremely soluble in acid and in NH_4OH. Hence it can be precipitated only from distinctly neutral solutions. This is readily accomplished by floating on the top of the slightly acid solution a little dilute NH_4OH. A neutral zone will form between the two layers and on the line of contact the colored precipitate will appear.

Unless Res. 10 is washed free from HCl, the test for As may be obscured by the precipitation of AgCl. If such is the case, make the solution slightly acid with HNO_3 and filter until clear. Upon the acid filt. float NH_4OH, adding more $AgNO_3$ if necessary, and look for the indication of As on the line of contact.

ANALYSIS OF RESIDUE 10 WHEN GOLD OR PLATINUM MAY BE PRESENT.

B. *If Res. 10, from page 256, is dark, i. e., probably contains Au or Pt.* Puncture the filter and wash into a test-tube with 10–15 ccm. $(NH_4)_2CO_3$. Shake vigorously for a few minutes, filter and wash.

<table>
<tr><td colspan="2">Res. 11. Au_2S_3, PtS_2.
Dissolve in as little aqua regia as possible and evaporate to dryness to remove excess of acid. Boil out with 15 ccm. water and divide into three portions.</td><td colspan="2">Filt. 11. Make faintly acid with HNO_3, pass H_2S if necessary to obtain a prec., filter and wash.</td></tr>
<tr><td>A (1) Add a few drops of a freshly prepared $FeSO_4$ solution.
Dark prec., metallic Au, indicates Au.
A (2) Dilute to 50 ccm. Add a single drop of $SnCl_4$ and a drop or two of $SnCl_2$.
Purple or brown color, metallic Au, indicates Au.</td><td>B. Add 5–10 drops of KCl and a volume of alcohol twice as great as the solution.
Yellow prec., K_2PtCl_6, indicates Pt.</td><td>Prec. 12.
As_2S_5.
Yellow prec., indicates As.
To confirm, treat as Res. 10 as directed under A, page 256.</td><td>Filt. 12.
Reject.</td></tr>
</table>

DISCUSSION OF THE ANALYSIS OF RESIDUE 10 WHEN GOLD OR PLATINUM MAY BE PRESENT.

If either Au or Pt be present in appreciable amounts, Res. 10 will be distinctly dark in color, for the sulfids of these metals are black. A slight darkening of the normal yellow color of Res. 10, however, may be due to sulfur which separates when the ammonium polysulfid extract is acidified and which, under these conditions, is often somewhat discolored.

The separation of As from Au and Pt depends upon the solubility of the sulfids of arsenic in $(NH_4)_2CO_3$, according to the equation:

$$As_2S_5 + 3(NH_4)_2CO_3 \rightarrow (NH_4)_3AsS_4 + (NH_4)_3AsSO_3 + 3CO_2$$

Ammonium thioarsenate and the arsenate in which only a quarter of the oxygen has been replaced by sulfur both decompose, when acidified, with the formation of As_2S_5 which may be confirmed by the previous tests. See page 256.

The action of aqua regia on the sulfids of gold and platinum converts them into soluble chlorids. The tests for gold depend upon the ready reduction of its salts to the metallic condition. Ferrous salts precipitate gold according to the equation:

$$2AuCl_3 + 6FeSO_4 \rightarrow 2Au + 2FeCl_3 + 2Fe_2(SO_4)_3$$

Similarly, stannous salts precipitate gold in a very finely-divided condition, according to the equation:

$$2AuCl_3 + 3SnCl_2 \rightarrow 2Au + 3SnCl_4$$

This precipitate, known as the "Purple of Cassius," always contains some stannous oxid, SnO.

The platinic chlorid, $PtCl_4$, formed by the action of aqua regia upon PtS_2, unites immediately with the HCl present in the aqua regia mixture to form hydrochlorplatinic acid, H_2PtCl_6. The potassium salt of this acid is somewhat soluble in water but much less so in alcohol and, on the addition of the latter reagent, the yellow precipitate, K_2PtCl_6, falls, indicating Pt. (See pages 74 and 235.)

DETECTION OF INTERFERING SUBSTANCES.

Evaporate a small portion of Filt. 4 to dryness in a small evaporating dish and desiccate at 110°–120°. Designate this dried res. as Prec. 13. Divide.

A. If an indication has not been given during the desiccation, heat in porcelain a portion of Prec. 13 with conc. H_2SO_4 until white fumes of SO_3 appear.

Carbonization, evidenced by darkening and "odor of burned sugar," indicates **carbonaceous matter.**

Boil out the remainder of Prec. 13 with HCl and filter.

B. Prec. 14. Heat before the blowpipe in a bead of $NaPO_3$.*

An insoluble skeleton, $\mathbf{SiO_2}$, indicates $\mathbf{H_2SiO_3}$.

Filt. 14. Divide into two portions:

C. To the smaller portion of Filt. 14 add a few drops of conc. HNO_3 and evaporate to dryness. Boil out the res. with 5–10 ccm. of water to which a drop or two of HNO_3 has been added.

To 5 ccm. of $(NH_4)_2MoO_4$ solution, add a few drops of the extracted solution and *warm slightly*.

Yellow prec., $\mathbf{(NH_4)_3PO_4 \cdot 12MoO_3}$, indicates $\mathbf{H_3PO_4}$.

If a yellow prec. does not form, add 1–2 ccm. of the extracted solution to the molybdate and *warm*.

If no prec. appears, test all of the extract in the same way.

D. To the larger portion of Filt. 14 add solid Na_2CO_3 to alkaline reaction and somewhat in excess, then boil thoroughly. Filter, acidify the filt. *slightly* with $H(C_2H_3O_2)$ and add an equal volume of saturated $CaSO_4$ solution.

White prec., $\mathbf{CaC_2O_4}$, indicates $\mathbf{H_2C_2O_4}$.

DISCUSSION OF THE DETECTION OF INTERFERING SUBSTANCES.

Certain substances interfere with the separation and detection of some of the metals. So long as the solution is acid with HCl and a considerable concentration of H ions is present, the reactions noted below do not take place. On making the solution ammoniacal or faintly acid with acetic acid, these substances begin to interfere and, therefore, must be removed before proceeding further with the analysis.

Organic bodies containing the hydroxyl radicle, such as sugar, starch, tartaric, citric and other acids, prevent the precipitation of ferric iron, aluminum and, to a smaller extent, of base-forming chromium as hydroxids or basic acetates. Complex bodies are formed which do not separate the simple metallic ions to an extent sufficient to cause precipitation.

If silicic acid, H_2SiO_3, is present, ammonium silicate will begin to form as soon as the solution is made nearly or quite alkaline with $(NH_4)_2CO_3$ or NH_4OH as in the analysis of Groups II–IV. Ammonium hydroxid is a weak base and silicic acid one of the weakest of acids, hence the salt is completely hydrolyzed and separates silicic acid as a white gelatinous precipitate which is likely to be mistaken for aluminum hydroxid or other white precipitate.

---

* Sodium meta-phosphate, $NaPO_3$, is usually prepared in small amounts as needed by the ignition of microcosmic salt, $H(NH_4)NaPO_4$. A small loop of platinum wire is heated and brought in contact with the microcosmic salt crystals which adhere to it. On heating, NH_3 and H_2O are driven off, leaving a clear, colorless bead of $NaPO_3$. By pressing the hot bead upon the substance to be tested, a sufficient quantity will adhere to give the reaction on heating. The skeleton of silica is more noticeable during the heating than subsequently, since it spins about in the bead under the influence of the blowpipe flame. (See page 78.)

Phosphoric and oxalic acids form insoluble salts with every metal still present in solution with the exception of the alkalies. Some of these compounds will precipitate in the presence of acetic acid but all will fall as soon as the solution is made ammoniacal. Unless these acids are removed, therefore, members of Groups II–IV may be precipitated in the wrong place in the analysis and thus introduce confusion.

A. Most non-volatile organic substances decompose when heated with the loss of water and the separation of free carbon. This " carbonization " or " charring " may be noted during the preliminary evaporation to dryness inasmuch as the sides of the dish above the liquid usually become heated sufficiently high to cause decomposition. Hot concentrated H_2SO_4 tends to extract water and thus aids the decomposition.

B. Silicic acid, H_2SiO_3, if present in solution, becomes dehydrated during the desiccation, forming the insoluble anhydrid, SiO_2, which constitutes the residue left after extracting with HCl. Heated in a bead of $NaPO_3$, no reaction takes place. Sodium meta-phosphate dissolves base-forming oxids with the formation of ortho-phosphates which fuse to a clear glass but non-volatile, infusible, acid-forming oxids, like SiO_2, remain undissolved as an opaque residue. (See page 136.)

C. In the present scheme of analysis, compounds containing phosphorus are separated and detected only after the phosphorus has been oxidized to the pentavalent condition and exists as ortho-phosphoric acid, H_3PO_4, for other forms do not respond to the reactions given. Evaporation with conc. HNO_3 accomplishes the oxidation and hydration is brought about by boiling with the dilute acid.

The test for H_3PO_4 depends upon the fact that in the presence of a large excess of molybdic acid, H_2MoO_4, phosphoric acid unites with the anhydrid, MoO_3 to form a complex acid. In the presence of $\overset{+}{NH}_4$ ions, ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, is formed, a compound insoluble in HNO_3. This yellow precipitate will come down slowly in the cold but slight warming will hasten its formation. *Even moderate heating is to be avoided*, however, as it tends to dehydrate molybdic acid and separate the straw-colored anhydrid. It is necessary that the proportions of Mo to P be at least 12:1 for otherwise compounds containing less Mo will form which are soluble. Hence the necessity of adding only a drop of the solution to be tested to 5 ccm. of $(NH_4)_2MoO_4$ in order to prevent the possibility of an excess of H_3PO_4, even should it be present in considerable amounts in the solution. The test is extremely delicate and serves to detect traces of phosphoric acid.

D. The addition of Na_2CO_3 to the filtrate precipitates all the metals present in solution either as carbonates or as insoluble salts of other acids present. On boiling the mixture, however, the latter are all transposed into carbonates of the metals and soluble sodium salts of the acids present. By this treatment, therefore, all bases except the alkalies are removed while the acids remain in solution. The addition of a solution of $CaSO_4$ (soluble in 500 parts of H_2O) introduces $\overset{++}{Ca}$ ions in such concentration that only highly insoluble calcium salts can be precipitated. Acetic acid prevents the formation of the phosphate, carbonate and similar salts and only the oxalate (soluble in 140,000 parts of H_2O and insoluble in acetic acid) can precipitate.

REMOVAL OF INTERFERING SUBBSTANCES.

A. If **no interfering substances** are detected, proceed with the analysis of Filt. 4 as directed on page 264.

B. If **carbonaceous matter** or **oxalic acid, $H_2C_2O_4$**, or both are detected, evaporate to dryness. Grind the dried residue in a mortar with 4–5 times its bulk of solid NH_4NO_3. In a porcelain crucible fuse enough NH_4NO_3 to cover the bottom and add the mixture in small portions, so regulating the temperature as to keep the contents of the crucible in a state of gentle fusion. When quiet fusion of the melt indicates that the oxidation is complete, raise the temperature somewhat to drive off most of the NH_4NO_3, cool and extract with hot water, adding a little HCl if necessary. Designate this solution as Filt. 15. If it is colorless (*i. e.,* does not contain $H_2Cr_2O_7$) and is free from H_2SiO_3, proceed according to the directions for the analysis of Filt. 4 on page 264. If Filt. 15 is somewhat yellow in color and a small portion when tested according to A (2), page 266, indicates $H_2Cr_2O_7$, concentrate to 5–10 ccm. Add an equal volume of conc. HCl and boil to reduce the chromium from the acid-forming to the base-forming condition. The reduction is indicated by a change in color from yellow to deep green. The completion of the reaction may be hastened by the addition of a few drops of alcohol. Remove most of the HCl by evaporating nearly to dryness and dissolve in water. Designate this solution as Filt. 16 and (if free from H_2SiO_3) proceed according to the directions for the analysis of Filt. 4 on page 264.

C. If **silicic acid, H_2SiO_3**, is indicated, evaporate to dryness in the presence of HCl and desiccate at 110–120°. Boil out with water and a little HCl and carefully decant the liquid from the insoluble residue, pouring it through a filter. Wash the residue by decantation with hot water and pour the washings through the filter.

Res. 17. Dry and transfer to a platinum crucible. Add a few drops of HF and about 1 ccm. of conc. H_2SO_4 and heat under a hood until fumes of SO_3 are no longer given off. If an appreciable residue is left, boil out with HCl and pour off the solution through a filter. Res. 18. If appreciable, fuse in platinum with 3–4 times its bulk of a mixture of Na_2CO_3 and K_2CO_3. After the melt becomes clear and fuses quietly, cool and boil out with water. Filter.	Filt. 17. After the addition of Filt 18, proceed as directed under Filt. 4, page 264. Filt. 18. Add to Filt. 17.

Res. 19. Wash with hot water, extract with HCl and filter.	Filt. 19. Reject.

Res. 20. If any, reject.	Filt. 20. Test for members of Group IV as directed under Filt. 23, page 270.

D. **Phosphoric acid, H_3PO_4**, if present, is removed in the separation of Group II as directed on page 264.

DISCUSSION OF THE REMOVAL OF INTERFERING SUBSTANCES.

B. The removal of oxalic acid and of carbonaceous matter in general depends upon the oxidation of these substances to CO_2 and H_2O. Nitrates are very satisfactory oxidizing agents, under these conditions the NH_4 rather than the Na or K salt being preferable, since it introduces no metallic element into the solution. (Tests are made for the presence of NH_4 salts before beginning the systematic analysis. See page 249.) During this fusion, Cr (if present) will be oxidized into the higher or acid-forming condition. Since the separation of this element depends on its being in the base-forming condition it must be reduced. This is accomplished by boiling with conc. HCl, chlorin being liberated according to the reaction:

$$H_2Cr_2O_7 + 12HCl \rightarrow 2CrCl_3 + 7H_2O + 3\mathit{Cl}_2$$

In the presence of the strong oxidizing agent, dichromic acid, HCl plays the part of a reducing agent (see page 49) but it is not readily oxidized and boiling for some minutes is necessary to complete the reaction. Alcohol, a strong reducing agent, is usually added to hasten the action (see pages 47 and 192) and is oxidized according to the equation:

$$H_2Cr_2O_7 + 6HCl + 3H_6C_2O \rightarrow 2CrCl_3 + 3H_4C_2O + 7H_2O$$

The product of the reaction, aldehyde, H_4C_2O, being volatile, may be removed by boiling from the solution, together with any unchanged alcohol.

If silicic acid be present during this fusion, insoluble silicates of some of the metals present may be formed which will not be decomposed by HCl and therefore require the treatment indicated under Res. 17.

C. Silicic acid is removed from solution by drying or desiccating at 110–120°, at which temperature it dehydrates forming the insoluble anhydride, SiO_2. If the desiccation is properly performed, silicic acid may be removed so completely that it will not interfere with the further analysis of the solution. If, however, the desiccation is imperfect, silicic acid may pass into Filt. 17, in which case this must be evaporated and desiccated a second time. Heating higher than 120° must be avoided, for, above this temperature, the SiO_2 first formed may react with metallic chlorids present to form soluble silicates and thus introduce silicic acid into the filtrate.

$$\mathbf{2NaCl} + \mathbf{SiO_2} + H_2O \rightarrow \mathbf{Na_2SiO_3} + 2\mathit{HCl}$$

A very satisfactory way to maintain the temperature necessary for desiccation and yet prevent overheating is to fan the evaporating dish with a Bunsen flame, stirring the drying residue constantly with a glass rod and breaking up any lumps that tend to form, until a fine dry powder is obtained.

Silicic anhydrid and all silicates are decomposed by HF with the formation of volatile SiF_4 (see page 135). On heating Res. 17 with HF and H_2SO_4, all Si will be driven off and, if the analysis has been properly performed up to this point, there will usually be only an inappreciable amount of material left as Res. 18. The sulfates of Ba, Sr and Ca may sometimes be present in considerable quantities, however, having been formed, either by incomplete removal of H_2S from Filt. 4 (see page 253) and its subsequent oxidation into H_2SO_4, or by the decomposition by means of HF and H_2SO_4 of insoluble silicates of these same metals, the silicates having been formed, possibly, during the fusion as indicated in B. If this be the case, fusion with an alkaline carbonate transposes them into carbonates of Ba, Sr and Ca and sulfates of the alkali metal (see page 69). Extraction with water removes the latter after which the carbonates may be dissolved by treating with HCl.

SEPARATION OF GROUP II.

To filt. 4, freed from H_2S, add a little HNO_3, boil and filter, if necessary.

RES. 21.* **$BaSO_4$, $SrSO_4$, $CaSO_4$.** Treat as directed for Res. 18 on page 262.	FILT. 21. Divide into two unequal portions.

A. To a small portion add 2–3 ccm. NH_4Cl, if it is not already present in sufficient amount,† make faintly alkaline with NH_4OH and boil. A prec. indicates the presence of Group II (or Groups III or IV as phosphates). *If no prec. forms,* proceed with the separation and analysis of Group III as directed on page 268.

B. *If a prec. forms in A,* add 5–10 ccm. NH_4Cl, if it is not already present in sufficient amount.† Add $(NH_4)_2CO_3$ until the first formation of a prec. indicates the neutralization of the solution. If the prec. which falls is not colored reddish-brown, add $FeCl_3$ until such a prec. does form on the further addition of a few drops of $(NH_4)_2CO_3$. Prevent the formation of any large amount of prec. by dissolving in HCl after each addition of $(NH_4)_2CO_3$ if the prec. is not of the right color. When sufficient $FeCl_3$ has been added, dissolve the prec. in the *smallest possible amount* of HCl and add 10 ccm. of $NH_4(C_2H_3O_2)$. Pour the resulting deep red solution into 400–500 ccm. of boiling water and maintain the boiling temperature until a reddish-brown prec. forms. Filter hot.

PREC. 22. *Group II.* **Al, Cr and Fe as basic acetates. ($FePO_4$,** if H_3PO_4 is present.) Proceed as directed on page 266.	FILT. 22.‡ *Groups III–V.* See page 268.

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* This res., if any, is due to the incomplete removal of H_2S and its subsequent oxidation to H_2SO_4. If the analysis has been performed carefully as directed, there should ordinarily be no Res. 21.

† Sufficient NH_4Cl will ordinarily be formed during the course of an analysis from the neutralization of HCl with NH_4OH or $(NH_4)_2CO_3$.

‡ Filt. 22 should be free from Fe (and Al and Cr also) and when acidified with HCl, should give no test with $K_4(Fe=C_6N_6)$ (see page 227). If Fe should be indicated, the separation has not been satisfactorily performed, owing, probably, to the presence of too much acetic acid, $H(C_2H_3O_2)$. Under these conditions the filtrate should be heated to boiling and a few drops of $(NH_4)_2CO_3$ added, not sufficient, however, to make the solution neutral or alkaline. Filter off the prec. and add to Prec. 22.

DISCUSSION OF THE SEPARATION OF GROUP II.

The separation of Group II depends on the fact that aluminum, chromium, and iron form basic acetates which are insoluble in the presence of a small concentration of acetic acid, whereas the metals of Groups III–V do not possess this property. For the formation of these compounds it is necessary that chromium be present in the trivalent base-forming condition and not in the higher oxidized acid-forming condition. Since ferrous iron does not form a basic acetate, it is necessary that iron be in the trivalent condition. If chromium be present in the original solution in the acid-forming condition and iron as a ferric salt, both will be reduced by H_2S in the presence of HCl, chromium to the trivalent and iron to the bivalent condition. In Filt. 4 it is necessary, therefore, to oxidize the iron without oxidizing the chromium. Nitric acid in dilute solution accomplishes this satisfactorily. If H_2S has not been previously boiled out completely (see page 252), it will be oxidized to H_2SO_4 by the HNO_3 and cause the precipitation of the metals of Group IV (Res. 21).

Inasmuch as a preliminary test may indicate the complete absence of Group II, it is advantageous to test Filt. 21 for the presence of this group before proceeding to the regular separation. The test as directed in A depends upon the fact that the hydroxids of aluminum, chromium and ferric iron are so little soluble in water that they may be precipitated by NH_4OH even in the presence of salts of ammonium which repress the ionization of the base (see page 31). The hydroxids of the metals of Groups III–V, being more soluble in water, cannot be precipitated by NH_4OH when the concentration of hydroxyl ions is reduced by the presence of ammonium salts. If H_3PO_4 is present, however, Groups III and IV may be precipitated as phosphates, since the phosphates of all of the metals, though soluble in acids, are insoluble in water and are precipitated as soon as the solution is made alkaline. Inasmuch as the basic acetate separation removes H_3PO_4 as well as the metals of Group II, if a precipitate forms in A, the regular procedure for the separation and analysis of Group II must be followed.

In order to make this separation satisfactorily, the solution should contain *as little acid as possible* in excess of the amount necessary to give an acid reaction. If the precipitate formed by $(NH_4)_2CO_3$ in B is dissolved in the *smallest possible amount* of HCl, on addition of $NH_4(C_2H_3O_2)$, acetic acid (and NH_4Cl) will be formed in place of the stronger HCl and on dilution to 500 ccm. the concentration of $\dot{H}$ ions will be sufficiently low to allow the acetates to hydrolyze and precipitate the insoluble basic salts. To what extent hydrolysis of the normal acetates of the type $Fe(C_2H_3O_2)_3$ will take place depends somewhat upon conditions. The composition of the precipitated basic acetates varies from $Fe(OH)(C_2H_3O_2)_2$ to $Fe(OH)_2(C_2H_3O_2)$. The filtration must be made while the solution is hot to prevent a reversal of the reaction and the solution of the basic acetates in the acetic acid formed by hydrolysis.

If H_3PO_4 be present, $FePO_4$ will form in preference to any other salt, since it is least soluble in water and acetic acid. This is indicated by the fact that on the addition of $FeCl_3$ to a solution containing phosphoric acid, straw-colored ferric phosphate is precipitated on neutralizing the acid rather than the red hydroxid. Only after all the H_3PO_4 present has united with the iron, does the hydroxid fall. That the excess of iron necessary for complete precipitation of chromium (see page 194) is present is indicated by the appearance of the red precipitate in B.

ANALYSIS OF GROUP II.

PREC. 22, from page 264. *Group II.* **Al, Cr,** and **Fe*** as **basic acetates.** (**$FePO_4$**, if H_3PO_4 is present.) Divide into two portions.

A. Mix one portion of the prec. with 5–10 ccm. water and add a little Na_2O_2, stirring or shaking the mixture to insure thorough treatment. Filter.

A yellow filt. indicates **Cr.**

Confirm by—

(1) *Acidifying carefully* a portion of the filt. with H_2SO_4. A transient blue color, $HCrO_4$, appearing as the solution becomes acid or on adding a few grains of Na_2O_2, confirms **Cr.**

(2) Evaporating a second portion of the filt. to dryness, cool, boil out with water, *faintly* acidify with $H(C_2H_3O_2)$ and add $Pb\ (C_2H_3O_2)_2$.

Yellow prec., **$PbCrO_4$**, confirms **Cr.**

B. Mix the second portion of the prec. with 5–10 ccm. water, add about half a gram of solid Na_2CO_3 and nearly as much solid $Ba(OH)_2$ and boil thoroughly. Filter into a test-tube, faintly acidify with HCl, make just alkaline with NH_4OH and boil until a prec. forms or the odor of NH_3 disappears.

Light white floccy prec., **$Al(OH)_3$**, more readily seen against a dark background, indicates **Al.**

To confirm, filter and wash the prec. into the tip of the paper. Tear off the tip of the filter containing the prec. and ignite strongly in platinum. Moisten with drop of *dilute* $Co(NO_3)_2$ and ignite again.

Blue color, **$Co(AlO_2)_2$**, confirms **Al.**

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* Special tests are made for the presence and condition of iron before beginning the Basic Analysis (see page 249). Since $FeCl_3$ is added to the solution to insure the complete precipitation of Cr (and to remove H_3PO_4, if present), it would obviously be absurd to test for the presence of Fe in this group.

DISCUSSION OF THE ANALYSIS OF GROUP II.

A. The test for Cr depends on the oxidation of the element from the trivalent, base-forming condition in which it is precipitated as the basic acetate, to the hexavalent acid-forming condition. Sodium peroxid, Na_2O_2, reacts with water to form H_2O_2 and NaOH, hence it is equivalent to H_2O_2 in alkaline solution. Under these conditions the oxidation of Cr stops with the formation of an alkali chromate, *e. g.*, Na_2CrO_4, which gives a yellow filtrate.

$$\mathbf{Cr(OH)_2.(C_2H_3O_2)} + NaOH \rightarrow \mathbf{Cr(OH)_3} + Na(C_2H_3O_2)$$
$$2\mathbf{Cr(OH)_3} + 3H_2O_2 + 4NaOH \rightarrow 2Na_2CrO_4 + 8H_2O$$

The confirmatory tests depend upon two reactions of chromium in the acid-forming condition. In acid solution, H_2O_2 oxidizes hexavalent Cr one step higher than in alkaline solution and forms a blue compound, probably $HCrO_4$. If Na_2O_2 was not added in sufficient quantity to form enough H_2O_2 for this test, it may be necessary to add a few grains after acidifying. A large excess should be avoided, however, because $HCrO_4$ and H_2O_2 interact as shown by the equation:

$$2HCrO_4 + 4H_2O_2 \rightarrow Cr_2O_3 + 5H_2O + 4O_2$$

In the presence of acid, Cr_2O_3 will be changed into the corresponding salt of base-forming Cr which, of course, will not give a blue color.

In order to prevent the oxidation of Na_2CrO_4 by H_2O_2 on acidifying with $H(C_2H_3O_2)$ in (2), the solution is evaporated to dryness to remove all H_2O_2, after which the regular test with the $\overset{++}{Pb}$ ion may be obtained.

B. The separation of Al from Cr depends on the solubility of the basic acetate of Al in boiling NaOH solution, whereas the corresponding salt of Cr, though soluble in the cold, is precipitated on boiling. For this reaction, the NaOH must be prepared by the action of Na_2CO_3 on $Ba(OH)_2$; for the ordinary reagent, especially after standing in glass bottles, always contains more or less of Al or compounds of silicic acid which may be confused with it. When made by the action of Na_2O_2 on water, the same impurities are present, also, and are likely therefore, to vitiate the test.

In the filtrate thus obtained, Al is present as sodium aluminate, Na_3AlO_3. Acidifying with HCl and making alkaline with NH_4OH effects the change from sodium aluminate, which is not decomposed by boiling, to ammonium aluminate, from which $Al(OH)_3$ may be precipitated on heating. (See pages 116 and 117.)

SEPARATION AND ANALYSIS OF GROUP III.

Heat Filt. 22 nearly to boiling, make slightly alkaline with NH_4OH,* add 2–3 ccm. colorless $(NH_4)_2S$ and filter. Test the filt. with a drop of $(NH_4)_2S$ to ascertain that precipitation is complete. Wash the prec. with warm water to which a little NH_4Cl and $(NH_4)_2S$ have been added.

Prec. 23. *Group III.* **CoS, NiS, MnS, ZnS.** Puncture the filter and wash the prec. into a test-tube with 10–20 ccm. of N·HCl.‡ Shake vigorously for 5–10 minutes to insure thorough treatment. If the prec. is light colored, *not otherwise,* heat may be applied to hasten solution. Filter and wash.

Filt. 23.† *Groups IV–V.* See page 270.

Res. 24. **CoS, NiS.** Heat a small portion in a borax-bead. Blue color, **$Co(BO_2)_2$**, indicates **Co.**

A. *If Co is not indicated,* dissolve the prec. in the least possible amount of aqua regia and make alkaline with Na_2CO_3.

Green prec., **$NiCO_3.Ni(OH)_2$**, indicates **Ni.**

B. *If Co is indicated,* dissolve the prec. in the least possible amount of aqua regia, evaporate nearly to dryness and dilute to 5 ccm. with water. Add Na_2CO_3 until a prec. begins to form and dissolve it again in the *least possible amount* of $H(C_2H_3O_2)$. Add 1–2 ccm. of $AlCl_3$ or alum solution and a small crystal of $K_3(Fe \equiv C_6N_6)$ and shake to hasten its solution. Add *conc.* NH_4OH equal to half the volume of the solution, shake thoroughly and filter.

Prec. 25. Maroon prec., **$Co_3(Fe \equiv C_6N_6)_2$**, confirms **Co.**

Filt. 25. To the filt. add a piece of solid NaOH the size of a bean and stand aside.

Black prec., **$Ni(OH)_2$**, forming about the NaOH, indicates **Ni.**

If no prec. appears on standing, boil until it does form or the odor of NH_3 is gone.

Filt. 24. Boil to remove H_2S, make alkaline with NaOH and filter.

Prec. 26. Light-brown prec., **$Mn(OH)_2$**, indicates **Mn.**

To confirm—

A. Dissolve a small portion of the prec. in 10–20 ccm. HNO_3 and boil, add about 1 gram PbO_2 and boil again. Stand to allow suspended matter to settle. Pink color, $HMnO_4$, indicates **Mn.**

B. Fuse the rest of the prec. with Na_2CO_3 and KNO_3 in a loop of platinum wire.

Green color, **$NaMnO_4$**, confirms **Mn.**

Filt. 26. Acidify faintly with HCl, add $Na(C_2H_3O_2)$ and pass H_2S

White prec., ZnS, indicates Zn.

Confirm by igniting the prec. on platinum, moisten with a drop of *dil.* $Co(NO_3)_2$ and ignite again.

Green color, **$CoZnO_2$**, confirms **Zn.**

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* Should a prec. form on the addition of NH_4OH, sufficient NH_4Cl is lacking. Dissolve the prec. in HCl and add NH_4Cl until no prec. appears when the solution is again made alkaline. If an analysis of Group III only be undertaken without the previous treatment to separate Groups I and II, 15 20 ccm. NH_4Cl must be added to the sol. before the addition of NH_4OH. In the course of a systematic analysis this is not usually necessary, as NH_4Cl will be formed in sufficient quantity during the previous reactions.

† If Filt. 23 is brown, it is due to NiS which is somewhat soluble in an excess of $(NH_4)_2S$, especially in the presence of considerable NH_4OH. Such a coloration is an indication that these reagents have been added in unnecessarily large amounts. To clear the filt., acidify with HCl, make *faintly* alkaline with NH_4OH and add, if necessary, a drop or two of $(NH_4)_2S$ to bring down NiS and filter.

‡ Normal HCl may be made by diluting the conc. acid with 12 volumes of water or the dil. acid with 3 volumes.

DISCUSSION OF THE SEPARATION AND ANALYSIS OF GROUP III.

The separation of Co, Ni, Mn and Zn as Group III depends upon the facts that the sulfids of these elements, although soluble in HCl, are insoluble in water, and secondly, that the hydroxids are not precipitated by NH_4OH in the presence of NH_4Cl, owing to the repression of the ionization of the weak base by its more readily dissociating salts (see page 31). For these reasons Co, Ni, Mn and Zn are not precipitated with the sulfids of Group I, Divs. B and C. The sulfids and hydroxids of Groups IV and V either do not form or are soluble under those ? conditions.

The precipitated sulfids are washed with dilute NH_4Cl solutions instead of pure water to prevent the formation of pseudo-solutions toward which these sulfids ? show a strong tendency. A few drops of $(NH_4)_2S$ are usually added to the NH_4Cl to prevent oxidation of moist CoS and NiS to soluble sulfates. For this reason the precipitate should be washed and treated with acid as quickly as possible.

The separation of Co and Ni from Mn and Zn depends on the relative insolubility of CoS and NiS in cold N HCl. Traces of these elements only dissolve with MnS and ZnS, not great enough to interfere with tests for the latter elements. As all the sulfids are more soluble in warm HCl, heat should be avoided unless a light-colored precipitate indicates that both Co and Ni are absent.

The detection of Co is not at all difficult even in the presence of many times as much Ni, the borax-bead test being exceedingly delicate. The detection of Ni in the presence of Co is more difficult. Aqua regia oxidizes both sulfids to sulfates, thus rendering them soluble. The separation by means of $K_3(Fe \equiv C_6N_6)$ depends upon the fact that in the presence of NH_4OH, a soluble nickel-ammonia ferricyanid is formed whereas the cobalt compound produced under the same conditions is insoluble. The maroon precipitate is a cobaltous ferricyanid containing ammonia, the proportion between the constituents apparently varying somewhat. The separation may be made most satisfactorily in solutions acid with acetic but not with mineral acids. The aluminum salt is added simply that the slimy $Co_3(Fe \equiv C_6N_6)_2$ may be entangled in the $Al(OH)_3$ precipitated by NH_4OH and thus readily filtered. The addition of NaOH to the filtrate transposes nickelous ferricyanid into $Ni(OH)_2$ and $Na_3(Fe \equiv C_6N_6)$. Since ferricyanids in alkaline solution act as oxidizing agents (see page 131), nickelous hydroxid is oxidized into nickelic hydroxid, $Ni(OH)_3$.

Filt. 24 is boiled to remove H_2S which, if present, would precipitate the sulfids again on making the solution alkaline. The separation of Mn and Zn depends upon the fact that of the hydroxids first precipitated by NaOH, zinc hydroxid can be made to play the part of an acid and will dissolve in an excess of an alkaline hydroxid to form soluble zincates (see page 103). Manganese hydroxid will not act as an acid and is insoluble under the same conditions. The addition of HCl to the alkaline zincate sets free ZnO_2H_2 and then causes it to play the part of a base again, in which condition it may be precipitated as a metallic sulfid.

Boiling with HNO_3 and PbO_2 oxidizes $Mn(OH)_2$ from the divalent base-forming condition into the heptavalent acid-forming condition, the change being indicated by the pink color of the solution. The test is very delicate and but little $Mn(OH)_2$ should be used as 1 gm. of PbO_2 will not be sufficient to oxidize a large amount of the precipitate.

A similar oxidation takes place on fusion with Na_2CO_3 and KNO_3 but in the presence of alkalies proceeds only as far as the green hexavalent manganates.

SEPARATION AND ANALYSIS OF GROUP IV.

Heat to boiling Filt. 23 (which should contain NH_4Cl and be alkaline with NH_4OH[*]), add 5–10 ccm. $(NH_4)_2CO_3$,[†] boil for a moment, add a few drops of $(NH_4)_2CO_3$ again and filter immediately.

Prec. 27. *Group IV.* **$BaCO_3$, $SrCO_3$, $CaCO_3$.** Treat on the paper with as little $H(C_2H_3O_2)$ as will suffice to dissolve the prec. and wash through the filter into a test-tube. Add a *few drops* of $K_2Cr_2O_7$ and filter.

Filt. 27. *Group V.* See page 272.

Prec. 28. Yellow prec., **$BaCrO_4$**, indicates **Ba.**

To confirm, dissolve in HCl.

A. Heat on platinum wire. Green flame confirms **Ba.**

B. Add an equal volume of saturated $CaSO_4$ solution.

White prec., **$BaSO_4$** confirms **Ba.**

Filt. 28. Make alkaline with NH_4OH, heat to boiling, add $(NH_4)_2CO_3$, filter and wash until yellow color has entirely disappeared.

Prec. 29. **$SrCO_3$, $CaCO_3$.** Dissolve in as little HNO_3 as possible and evaporate nearly to dryness. Add 5–10 ccm. amyl alcohol and dehydrate by boiling until the vapor of the alcohol will burn quietly at the mouth of the test-tube, taking care that the volume does not become less than 5 ccm.

If no res. is left, Sr is absent. Prec. 29 must have been **$CaCO_3$.** Confirm by testing as directed under Filt. 30.

If a res. is present, it indicates **Sr**, or possibly traces of **Ca.** Carefully decant the liquid from the res. and pour through a dry filter.

Filt. 29. Reject.

Res. 30. Ignite the res. in the test-tube gently, cool, dissolve in a drop or two of HNO_3, treat with 5–10 ccm. of amyl alcohol and dehydrate as before.

Light colored res. indicates **Sr.** Moisten with a drop of HCl and heat on platinum wire.

Brilliant crimson flame confirms **Sr.**

Filt. 30. Dilute with an equal volume of ordinary ethyl alcohol and add H_2SO_4.

White, floccy prec.,[‡] **$CaSO_4$**, indicates **Ca.**

To confirm, filter, moisten prec. with HCl and heat on platinum wire.

Orange flame confirms **Ca.**

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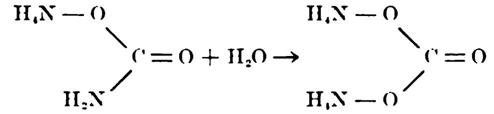
[*] In performing a partial analysis of Group IV alone or with Group V, 3–5 ccm. of NH_4Cl should be added and the solution made alkaline with NH_4OH before treating with $(NH_4)_2CO_3$.

[†] Commercial $(NH_4)_2CO_3$ consists mainly of a mixture of acid ammonium carbonate and ammonium carbonate, both of which form soluble salts with the metals of this group. On heating to 60°, the carbamate is changed into the carbonate according to the equation:



The NH_4OH added to the solution before precipitation changes the acid carbonate into normal carbonate and makes the solution alkaline. Were $(NH_4)_2CO_3$ added to an acid solution, CO_2 would be liberated which would tend to form acid carbonates, also.

[‡] A faint cloudiness may be due to Sr.

DISCUSSION OF THE SEPARATION AND ANALYSIS OF GROUP IV.

The separation of Group IV depends on the relative insolubility of the carbonates of Ba, Sr and Ca, even in the presence of NH_4Cl. Under these conditions Mg forms a complex salt, $(NH_4)_2MgCl_4$, which does not separate $\overset{++}{Mg}$ ions in sufficient concentration to precipitate the carbonate when treated with $(NH_4)_2CO_3$. The carbonates of the alkalies are all readily soluble and with Mg pass through into the filtrate.

Precipitation from boiling solution and subsequent short boiling changes the amorphous precipitate into the crystalline form in which condition it is much more readily filtered. Boiling should not be continued longer than is necessary to effect the change as, otherwise, a reversion of the reaction by which the carbonates were precipitated takes place, owing to the decomposition of $(NH_4)_2CO_3$ into NH_3, CO_2 and H_2O which are boiled out of solution (see page 76). In this way a considerable amount of the precipitate may dissolve making the separation of Group IV far from exact. The following equations serve to illustrate this point:

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow \mathbf{CaCO_3} + 2NH_4Cl$$
$$\mathbf{CaCO_3} + 2NH_4Cl \rightarrow CaCl_2 + (NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$$

The separation of Ba from Sr and Ca depends on the fact that a solution of $K_2Cr_2O_7$ contains sufficient $\overset{=}{CrO_4}$ ions (see page 195) to precipitate $BaCrO_4$ but not $SrCrO_4$ or $CaCrO_4$. In alkaline solution, the ions $\overset{=}{Cr_2O_7}$ change into $\overset{=}{CrO_4}$ ions which may precipitate $SrCrO_4$ from concentrated solutions, hence the precipitation is made in the presence of acetic acid in which $BaCrO_4$ is not appreciably soluble.

Before separating Sr from Ca, it is necessary to remove chromates entirely; for these salts are insoluble in amyl alcohol and will remain with the Sr. Ca and Sr are therefore reprecipitated as carbonates and washed until the yellow color has entirely disappeared. Their separation depends on the fact that anhydrous $Sr(NO_3)_2$ is insoluble in boiling amyl alcohol while $Ca(NO_3)_2$ is soluble. Dehydration of the nitrates is readily accomplished by boiling with amyl alcohol because its boiling-point (128–132°) is higher than that of water. As long as water is present, the alcohol will boil with slight explosions and the vapor will not burn quietly.

By the action of free HNO_3 (a little of which is always present after dissolving the carbonates) on amyl alcohol, certain organic acids may be formed capable of uniting with Ca and preventing solution. Any basic nitrate of Ca, which may sometimes form, is likewise insoluble. Hence it is necessary to repeat the extraction with amyl alcohol to be certain that only Sr remains undissolved. Ignition of the residue is necessary to decompose the salt of any organic acid into the carbonate which is then converted into nitrate by HNO_3.

Traces of Sr may dissolve in amyl alcohol and give a slight cloudiness to the filtrate. This will scarcely interfere with the test for Ca inasmuch as $CaSO_4$ comes down in a heavy flocculent precipitate under these conditions. Amyl alcohol and water are not miscible. Ethyl alcohol mixes readily with either. By adding an equal volume of the latter solvent a homogeneous mixture may be obtained when dilute H_2SO_4 is added.

Al. Zn. As.

ANALYSIS OF GROUP V.

To Filt. 27 add a few drops of $(NH_4)_2SO_4$ and $(NH_4)C_2O_4$, warm and filter if necessary.

Prec. 31.* $BaSO_4$, CaC_2O_4, ($SrSO_4$).	Filt 31. Divide into two portions.
A. Add HNa_2PO_4. White prec., **$Mg(NH_4)PO_4$**, indicates **Mg.** Confirm by dissolving the prec. suspended in the liquid in the least possible amount of HCl, heat to boiling and *neutralize carefully* by the addition of NH_4OH, *drop by drop*. The reappearance of the prec. in crystalline form confirms **Mg.**	B. Evaporate to dryness and ignite until ammonium salts are entirely removed,† *i. e.*, white fumes cease to be given off. (1) *If Mg. was not found in A*, test for the alkali metals as directed under Filt. 33. (2) *If Mg was found in A*, boil out the ignited res. with a little water, add $Ba(OH)_2$ until the solution is alkaline to litmus and filter.

Prec. 32. **$Mg(OH)_2$**. Reject.	Filt. 32. Add H_2SO_4 until the solution is ***just acid*** to litmus, warm and filter.
Prec. 33. **$BaSO_4$**. Reject.	Filt. 33. Evaporate almost to dryness and test for K, Na and Li by heating on a platinum wire in a Bunsen flame.

Examined with an ordinary spectroscope Na, if present in solution, gives a single yellow line of great intensity.‡ Li gives a crimson line a short distance to the left of the Na line. K gives a red line still further to the left of the Na line than is the Li line and a blue line far toward the right end of the spectrum. See Table of Spectra, frontispiece.

Examined without the aid of the spectroscope **Na** gives an intensely **yellow flame, Li** a **carmine flame** and **K** a **violet flame.**§

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* If this prec. is appreciable and Prec. 27 was unsatisfactory in quantity owing to the solvent action of NH_4Cl on the carbonates, Prec. 31 may be rendered soluble by fusion with Na_2CO_3 as directed on page 262. The melt, after extraction with boiling water, may be treated as Prec. 27, and examined for members of Group IV.

† Ammonium salts are introduced during the course of the analysis, hence must be tested for before beginning the regular analysis (see page 249). If Na or K have been introduced in the preparation of the solution (see page 241) or otherwise, their detection in Group V is without significance. Special treatment must be given in order to ascertain their presence. The original substance may extracted with boiling water or HCl and the resulting solution tested, or, in the case of insoluble silicates, the method given on page 242 may be followed.

‡ Because of the extreme delicacy of this method of detection, the Na line is ever-present with greater or less intensity even when Na is not present in solution in appreciable quantity.

§ In the presence of Na, the K flame is masked and cannot be detected with the unaided eye. Viewed through a potassioscope (see page 57), however, it is readily distinguishable.

DISCUSSION OF ANALYSIS OF GROUP V.

Group V consists of those metals that are not precipitated as chlorids, sulfids, basic acetates or carbonates under the conditions of the analysis and are therefore left together as a soluble residue after each of the preceding groups has been precipitated.

Magnesium differs in its chemical nature from the other members of this group and can be separated from them by precipitation as the phosphate, for phosphates of the alkali metals only are soluble. This reaction for the detection of Mg is of value only in the absence of other metals, for every one of the metals considered in the present scheme of analysis will form a precipitate when treated with HNa_2PO_4 in ammonical solution with the exceptions of As and Sb. Of these the metals of Group IV only are likely to be present in appreciable quantities, owing to the solvent action of NH_4Cl on the carbonates of Ba and Ca especially. The sulfate and oxalate ions remove these metals from solution so completely, however, that there is no possibility of precipitating them as phosphates, for $BaSO_4$ and CaC_2O_4 are much less soluble than the corresponding phosphates. Strontium as sulfate or oxalate is not likely to be present unless Prec. 31 be very considerable in quantity thus indicating that Prec. 27 was not brought down under satisfactory conditions. Strontium carbonate is much less soluble in water than either $BaCO_3$ or $CaCO_3$ and, therefore, is much less affected by NH_4Cl.

The absence of all other metals being thus assured, any precipitate which falls after introducing the $\overline{\text{PO}}_4$ ions must be due to Mg. Small amounts of this phosphate are slow in separating from supersaturated solutions, however, but, on standing over night, a crystalline precipitate will settle. If the inside of the glass vessel holding the solution be scratched with a glass rod, the crystals tend to collect along the roughened surface and may be more readily detected.

The exceedingly close chemical similarity between K, Na and Li renders any separation of these elements difficult. Fortunately, however, they may be readily detected by their characteristic flame colors. In the spectroscopic examination, both Mg and NH_4 salts tend to make the indications less distinct and they are removed therefore. All ammonium salts are volatile and may be driven off by ignition. After the removal of NH_4Cl, Mg may be precipitated by the OH ion, for the introduction of which, obviously, neither NaOH, KOH or NH_4OH will serve. Barium hydroxid, $Ba(OH)_2$, is used because any excess may be readily and completely removed by the addition of H_2SO_4. In the resulting filtrate, after concentration, the alkali metals may be readily detected spectroscopically. Inasmuch as the spectroscope reveals the presence of exceedingly minute quantities of these elements and since Na salts are present everywhere as a fine dust in the air, it is necessary to judge carefully the intensity of the indication in deciding whether or not Na salts are present in solution in appreciable quantities. This applies to the examination of the flame color with the unaided eye as well. If Na be present, the flame will be *intensely* yellow and the indication will be lasting.

THE ACID ANALYSIS.

Owing to the fact that anions show a much greater variety of reactions than do kathions, the Acid Analysis cannot be made as systematic as the Basic Analysis. The method of the Basic Analysis cannot be applied to the acids. The separation of the acids by precipitation into groups from which, by further analysis, each individual acid may be isolated and detected can not be accomplished satisfactorily. The method of the Acid Analysis is, in general, to test the prepared solution for the presence of each acid by individual tests. By certain preliminary reactions, however, the presence or absence of certain groups may be indicated. The classification is dependent mainly on the action of the $\overset{++}{\text{Ba}}$ and $\overset{+}{\text{Ag}}$ ions, supplemented by the action of certain reducing and oxidizing agents. The groups thus formed are not all mutually exclusive but certain acids may appear in two or more groups. Careful consideration of the implications of these preliminary tests and intelligent forethought will simplify and shorten the Acid Analysis very considerably.

Acids precipitated as insoluble salts by the addition of the **$\overset{++}{\text{Ba}}$ ion** to a neutral solution:

H_2SO_4, H_2SiF_6, HF, $H_2C_2O_4$, H_2SiO_3, $H_2Cr_2O_7$, H_2CO_3, H_3PO_4, H_3AsO_4, H_3AsO_3, H_3BO_3, H_2SO_3, $H_2S_2O_3$, $H_2(C_4H_4O_6)$.

Acids precipitated as insoluble salts by the addition of the **$\overset{+}{\text{Ag}}$ ion** to solutions acidified with HNO_3:

$H_3(Fe \equiv C_6N_6)$, $H_4(Fe = C_6N_6)$, HSCN, HCN, H_2S, HI, HBr, HCl, HOCl, HNO_2,* $H(C_2H_3O_2)$.*

Acids not precipitated under either of the above conditions, the barium salts being soluble in water and the silver salts in dilute nitric acid:

$H(C_2H_3O_2)$,* HNO_2,* HNO_3, $HClO_3$, $HClO_4$, $HMnO_4$, HOCN, H_2O_2.

---

* The silver salts of HNO_2 and $H(C_2H_3O_2)$ can be precipitated from concentrated solutions only.

PRELIMINARY TESTS FOR THE PRESENCE OF ACIDS.

(1) Acidify a portion of the *prepared solution* with HCl. A prec. of (a) sulfur, or (b) iodin indicates the presence of one or more of A or B.

A.

$H_2S_2O_3$.
H_2S_x.
H_2S + Oxidizing agents.

B

HI + Oxidizing agents.

Filter clear and add $BaCl_2$. White prec. indicates one or more of C.

C.

H_2SO_4.
~~H_2SiF_6.~~

Filter clear and boil to remove CO_2. Cool, add $CaCl_2$ and an equal volume of $Na(C_2H_3O_2)$. Prec. indicates one or more of D.

D.

HF.
$H_2C_2O_4$.
H_2SiO_3.
$H_2Cr_2O_7$ if prec. is yellowish.

Filter clear and make alkaline with $Ba(OH)_2$. Prec. indicates one or more of E.

E.

H_2CO_3. [illegible]	H_3AsO_3.	H_2SO_3.
H_3PO_4.	H_2SiO_3.	$H_2S_2O_3$.
H_3AsO_4.	H_3BO_3.	~~$H_2(C_4H_4O_6)$.~~

(2) Acidify a second portion of the *prepared solution* with HNO_3 and add $AgNO_3$. A prec. indicates one or more of F and possibly one or more of G.

Absence of a prec. indicates the absence of all of F but not necessarily of all of G.

F.—		G.—	H.—	I.—
$H_3(Fe\equiv C_6N_6)$.	HI.	HNO_2.	$H_4(Fe=C_6N_6)$.	HNO_3.
$H_4(Fe=C_6N_6)$.	HBr.	$H(C_2H_3O_2)$.	H_2S.	$HClO_3$
HSCN.	HCl.		HI.	$HClO_4$.
HCN.	~~HOCl.~~		HBr.	$HMnO_4$.
H_2S.				~~HOCN.~~
				~~H_2O_2.~~

If a prec. was obtained with $AgNO_3$, shake thoroughly to coagulate it and allow to settle. Pour off the liquid and wash the prec. by decantation. Treat the prec. with dil. NH_4OH and shake thoroughly. If the prec. is entirely dissolved, no member of H can be present.

(3) No prec. with $AgNO_3$ nor with $BaCl_2$ indicates the absence of all A, B, C, D, E and F. One or more of G or I may be present, however.

(4) Test for oxidizing acids: To 1–2 ccm. of the *prepared solution* add twice its volume of $MnCl_2$ in conc. HCl and warm gently. The appearance of a dark coloration (higher chlorids of manganese) is due to the presence of some oxidizing agent. One or more of J may be present. The absence of such a color proves the absence of all of J.

J. H_2O_2, HNO_2, HNO_3, HOCl, $HClO_3$, $HMnO_4$, $H_2Cr_2O_7$, $H_3(Fe\equiv C_6N_6)$.

(5) Test for reducing acids: Acidify a portion of the *prepared solution* with H_2SO_4 and add a single drop of dil. $KMnO_4$ solution. If color is not bleached after ten minutes, none of K is present.

K.—	
H_2S.	HI.
H_2SO_3.	HBr.
$H_2S_2O_3$.	H_3AsO_3.
HSCN.	HNO_2.
$H_4(Fe=C_6N_6)$.	H_2O_2.

If color is not bleached in the cold solution, heat nearly to boiling. If the color still remains none of L is present.

L.—
$H_2C_2O_4$.
$H_2(C_4H_4O_6)$.

If bleaching does not occur either hot or cold, one or more of M may be present but none of K or L.

M.—H_2SO_4, H_2SiF_6, HF, H_2SiO_3, $H_2Cr_2O_7$, H_2CO_3, H_3PO_4, H_3AsO_4, H_3BO_3, $H_3(Fe\equiv C_6N_6)$, HCN, HCl, HOCl, $H(C_2H_3O_2)$, HNO_3, $HClO_3$, $HClO_4$, $HMnO_4$, HOCN.

DISCUSSION OF THE PRELIMINARY TESTS FOR ACIDS.

While the salts of certain acids are stable in neutral or alkaline solution, the free acids are unstable and give evidence indicative of their presence. When the solution is acidified sulfur is separated (on standing) if thiosulfates or polysulfids are present, or sulfids together with oxidizing agents. Similarly iodids with oxidizing agents separate iodin. These acids constitute groups A and B.

Group C consists of those acids whose barium salts are insoluble in HCl, and group D of those whose barium or calcium salts are insoluble in acetic acid. By the addition of sodium acetate, the solution acid with HCl is changed to one acid with $H(C_2H_3O_2)$. Calcium chlorid is added inasmuch as the calcium salts of HF and $H_2C_2O_4$ are less soluble than the corresponding barium salts. Silicic acid may or may not come down in the presence of acetic acid, its action depending largely on the amount present.

Group E consists of those acids whose barium or calcium salts are precipitated from alkaline solutions, $Ba(OH)_2$ being used in preference to NH_4OH since the salts of the last four members of this group are appreciably soluble in the presence of ammonium salts. Sodium or potassium hydroxids always contain carbonates.

Group F contains the acids whose silver salts are highly insoluble in HNO_3. Hypochlorous acid appears in this group because its silver salt, although soluble in water, decomposes very readily, according to the equation:—

$$3AgOCl \rightarrow 2AgCl + AgClO_3.$$

Group G consists of those acids whose silver salts under the same conditions may be precipitated only from concentrated solutions. The acids of these two groups may be classified in another way, owing to the fact that the silver salts of certain of them are not readily soluble in NH_4OH. These are placed together, therefore, in group H. Silver bromid is appreciably, but usually not entirely, soluble in NH_4OH.

Group I consists of those acids whose barium salts are soluble in water and whose silver salts are not precipitated in the presence of HNO_3.

Individual tests must be made for each of the acids in the groups indicated to be present by these preliminary experiments unless the tests for oxidizing and reducing acids indicate that certain of them are not present.

Under the influence of oxidizing agents in general, HCl is oxidized to water and free chlorin. In concentrated HCl solution, the higher chlorids of manganese, $MnCl_3$ or $MnCl_4$ (see page 214), dark brown in color, may be formed and are capable of temporary existence. The acids which act as oxidizing agents under these conditions constitute group J. Ferricyanic acid gives a dark-drab, opaque solution appearing somewhat different from the other acids.

Many free acids act as reducing agents and will bleach a dilute solution of $KMnO_4$. Such as act in the cold are classed together in K while oxalic and tartaric acids usually require heating and constitute group L. Hydrocyanic acid may cause slight bleaching in hot, fairly concentrated solutions but most of the HCN will boil out unchanged and may be detected by its characteristic odor. Most acids do not have any reducing action and are classed as group M. Two bodies, H_2O_2 and HNO_2, because of their instability react readily with either oxidizing or reducing agents and therefore are found both in groups J and K. Although salts are much more stable than free acids, in general oxidizing and reducing agents cannot exist in the same solution.

If no test for any acid can be obtained, the original substance must have been an element or its oxid or hydroxid.

TEST FOR SULFURIC ACID.

Acidify a portion of the *prepared solution* with HCl, add $BaCl_2$ as long as a precipitate falls, filter, wash and dry the precipitate.[*] Mix with Na_2CO_3 and heat before the blowpipe upon charcoal. Remove the residue from the charcoal, place upon a silver coin and moisten with a drop of water.

A dark stain, Ag_2S, indicates the presence of H_2SO_4.

[*] Part of this precipitate may be used in testing for H_2SiF_6 (see next test).

TEST FOR HYDROSILICOFLUORIC ACID.

Acidify a portion of the *prepared solution* with HCl, add $BaCl_2$ as long as a precipitate falls, stand for ten minutes then filter, wash and *dry the precipitate thoroughly*. Heat in a test-tube with conc. H_2SO_4 and hold in the fumes evolved a loop of platinum wire containing a drop of water.

The formation of a white deposit, H_2SiO_3, in the water indicates the presence of H_2SiF_6.

TESTS FOR HYDROFLUORIC ACID.

(1) In a platinum crucible treat a small portion of the dry substance with warm conc. H_2SO_4 and cover with a watch-glass which has been previously coated with paraffine in which two or three scratches have been made with a knife blade.

On standing, etching of the glass where exposed to the fumes indicates HF.

(2) From a portion of the *prepared solution* acidified with HCl remove H_2SO_4 and H_2SiF_6 by treating with $BaCl_2$ and filtering. Warm the clear filtrate and add $CaCl_2$. Make the solution alkaline with $Ba(OH)_2$ and after a moment make *just acid* again with HCl.

A white precipitate, CaF_2, insoluble in dilute HCl, indicates HF.

Confirm by filtering and mixing the *dried precipitate* with an equal amount of a *dry* silicate. Treat with conc. H_2SO_4, exposing a rod moistened with water to the fumes evolved.

White precipitate, appearing as flecks in the drop of water, H_2SiO_3, confirms the test for HF.

DISCUSSION OF THE TEST FOR SULFURIC ACID.

In the presence of HCl the barium ion gives no precipitate except with sulfuric acid and hydrosilicofluoric acid (which see). The formation of a precipitate may indicate the presence of both of these acids or of one in the known absence of the other. Fusion with Na_2CO_3 on charcoal results in the reduction of the sulfate to the sulfid, which when moistened and brought in contact with metallic silver produces a dark stain of silver sulfid. Oxygen is absorbed from the air at the same time according to the equation:

$$\mathbf{4Ag} + 2Na_2S + \mathit{O_2} + 2H_2O \rightarrow \mathbf{2Ag_2S} + 4NaOH$$

DISCUSSION OF THE TEST FOR HYDROSILICOFLUORIC ACID.

Under the conditions of the experiment, $BaSiF_6$ (or $BaSO_4$) only can be precipitated. When the dried precipitate is heated with conc. H_2SO_4, H_2SiF_6 is liberated and decomposes into SiF_4 and HF, both of which are volatile. On coming in contact with water SiF_4 reacts with it to form silicic acid which appears as white flecks within the liquid (see page 133). The mixture in the test-tube *must be anhydrous* as otherwise this reaction will take place immediately and SiF_4 will never be volatilized.

DISCUSSION OF THE TESTS FOR HYDROFLUORIC ACID.

Test (1) depends on the corrosive action of HF on glass and other silicates (see page 199). It is a delicate test and on melting off the paraffine, etching of the glass will appear along the lines where the paraffine was scratched.

The separation of HF, as the second test, depends upon the fact that although barium fluorid will not come down in the presence of HCl, once precipitated it is not readily soluble in dilute HCl. Calcium fluorid is somewhat more insoluble in water and acid than barium fluorid. Since all other acids giving barium salts insoluble in water are distinctly weaker than hydrochloric acid, their salts will be readily dissolved away from the fluorids by HCl. Ammonium salts exert quite a solvent action on fluorids, however. By working with the *prepared solution* (made by boiling with sodium carbonate) and using barium hydroxid as base, all ammonium salts are avoided.

TESTS FOR SILICIC ACID.

(1) In a platinum crucible intimately mix some of the *dry substance* with an equal weight of powdered CaF_2, moisten with conc. H_2SO_4, and heat under the hood. Expose a film of water on a loop of platinum wire to the fumes evolved.

The formation of white flecks of silicic acid indicates the presence of **H_2SiO_3**.

(2) Acidify a portion of the *prepared solution* with HCl, evaporate to dryness and desiccate at 120° (see page 263). Extract by boiling with dilute HCl, pour off the solution from the residue, and wash by decantation. Heat some of the residue before the blowpipe in a sodium meta-phosphate bead (made by heating microcosmic salt).

The formation of an infusible "skeleton," **SiO_2**, not dissolving in the bead, indicates **H_2SiO_3**.

TEST FOR DICHROMIC ACID.*

Make a portion of the *prepared solution faintly acid* with HNO_3 and boil to remove CO_2. Make *just alkaline* with NH_4OH, add $CaCl_2$, warm and stand aside for 10–15 minutes, shaking vigorously from time to time to induce precipitation. Filter, acidify the clear filtrate *slightly* with HNO_3 and add $BaCl_2$. Filter again and to the clear filtrate add $Pb(C_2H_3O_2)_2$, and $Na(C_2H_3O_2)$ if necessary to effect precipitation.

A yellow precipitate, **$PbCrO_4$**, indicates **$H_2Cr_2O_7$**.

To confirm, filter and treat the precipitate on the filter paper with warm HNO_3, allowing the solution to filter through into a test-tube. Cool and add a few grains of Na_2O_2.

The appearance of a transitory blue color, due to $HCrO_4$, confirms **$H_2Cr_2O_7$**.

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[*] Chromic acid, H_2CrO_4, is unknown, for as soon as it is liberated from its salts, it loses water and passes into dichromic acid (see page 195).

DISCUSSION OF TESTS FOR SILICIC ACID.

All silicates are decomposed by HF with the formation of SiF_4, hence nothing will interfere with test (1) for silicic acid. Since silicon fluorid is decomposed by water, forming silicic acid and hydrofluoric acid (see page 133) the mixture in the crucible *must be kept anhydrous*. Concentrated sulfuric acid is added for this purpose as well as to liberate the HF.

The second test can be relied upon to detect silicic acid in solution under all circumstances (see page 135). If the dry substance is similarly treated, the skeleton indication will appear in most cases when silicic acid is present (see page 136); yet the indication is usually less definite, since the basic constituents of the original substances will dissolve, often rendering the bead turbid.

Inasmuch as silicic acid is usually detected during the Basic Analysis it will generally be unnecessary to make tests for it in the Acid Analysis.

DISCUSSION OF THE TEST FOR DICHROMIC ACID.

The presence of a chromate or dichromate is frequently indicated during the Basic Analysis by the change in color from yellow or red to green when the solution is treated with H_2S. Chromium, even if present in the acidic condition, is thus reduced to the basic condition (see pages 253 and 265), and is precipitated with the metals of Group II. If chromium is detected in the Basic Analysis, it does not follow, however, that it was originally present in the acid condition, hence the necessity for this test in the Acid Analysis. It is unnecessary to test a colorless solution for the presence of dichromic acid, however.

While a large amount of dichromic acid will make itself evident during both the Basic and Acid Analyses, when present only in small quantity, considerable care is required for its detection. Certain acids must be previously removed. Carbonates are first destroyed. Tartaric acid (which tends to hold up the precipitate of $PbCrO_4$) and other acids are precipitated as calcium salts in alkaline solution. Since ammonium salts exert a solvent action on tartrates, chromates and salts of other acids, the amount of NH_4OH introduced must be kept as small as possible. Calcium tartrate shows strong tendency to form supersaturated solutions and vigorous shaking is necessary to bring down a precipitate. From the filtrate once again acidified with HNO_3, the $\overset{++}{Ba}$ ion precipitates H_2SO_4. After filtering, the addition of $Pb(C_2H_3O_2)_2$ introduces the $\overset{++}{Pb}$ ion and changes the solution from one acid, with HNO_3 to one acid with $H(C_2H_3O_2)$, under which condition $PbCrO_4$ is precipitated. Sodium acetate affects the same change and represses the ionization of the acetic acid formed by the reaction. (See pages 27 and 31.)

If iodids be present, PbI_2 may be precipitated also as golden spangles. They are readily soluble in boiling water, however, and may thus be separated from the chromate. The confirmatory test is discussed on page 267.

TESTS FOR BORIC ACID.

(1) A. Moisten some of the dry substance with conc. H_2SO_4 and heat befo the blowpipe.

A characteristic green color indicates H_3BO_3 (*in the absence of Ba and C salts*).

B. *If a green color does not appear in A,* mix the finely powdered substance with CaF_2 and $KHSO_4$, moisten with a drop of water and heat in a loo of platinum wire, holding the bead at the edge and near the bottom of th Bunsen flame.

A green color indicates H_3BO_3 (*in the absence of Ba and Cu salts*).

(2) If the substance exists in solution, evaporate a portion to dryne add 3-4 ccm. of methyl alcohol and an equal volume of conc. H_2SO_4, and warm igniting the vapor (if necessary in the apparatus described on page 114).

A flame, green or edged with green when traces only are present, indicat H_3BO_3.

(3) Acidify a portion of the *original* or the *prepared solution* with HC Absorb in turmeric paper and dry at 100° (by placing on the side of a beak in which water is boiling), repeating this treatment several times if necessary

The appearance of a pink coloration turning dark green on treating wit alkalies indicates the presence of H_3BO_3.

TEST FOR CARBONIC ACID.

Treat some of the dry substance, or its solution *in water*, with H_2SO_4 and pas the gas evolved through "lime water," $Ca(OH)_2$.

A white precipitate, $CaCO_3$, indicates the presence of H_2CO_3.

If the indication is not obtained at first, warm, and, if necessary, add mor acid.

DISCUSSION OF TESTS FOR BORIC ACID.

In the flame test without the use of alcohol, it is necessary to distinguish carefully between barium or copper salts and compounds of boric acid, all of which color the flame green. Neither barium nor copper compounds are volatile under the conditions prescribed in Test (2), and therefore would not interfere in this way. While simple borates respond to Test (1) A very satisfactorily, some silicates containing boron are not sufficiently decomposed by H_2SO_4 to give this test for boric acid, but require the stronger action of HF formed from the interaction of acid potassium sulfate and calcium fluorid. Under these conditions volatile boron fluorid, BF_3, is formed which also colors the flame green.

For the discussion of Test (2) see page 114.

Oxidizing agents (except HNO_3) interfere with the turmeric-paper test for boric acid, by destroying the turmeric. Since hydriodic acid is readily decomposed by the oxygen of the atmosphere (see page 211) with the liberation of iodin which is a bleaching agent, the presence of iodids also interferes with this test. Iodids may be removed by treating the acid solution with potassium nitrite and boiling (see test for iodids, page 296), after which any oxidizing agents may be reduced in acid solution by treatment with sodium sulfite. (See page 185.)

DISCUSSION OF TEST FOR CARBONIC ACID.

If salts of carbonic acid be present in any appreciable amount, the fact will usually be indicated during the Basic Analysis as soon as the solution is acidified. Therefore, it will be unnecessary, generally, to make a direct test for carbonic acid during the Acid Analysis.

Some carbonates of metals forming insoluble sulfates are not readily decomposed by H_2SO_4, for the reason that the insoluble precipitate formed by H_2SO_4 covers over the dry substance and protects it from further action by the acid. If the dry substance does not dissolve and no test for carbonic acid is obtained, it may be desirable to substitute HCl and repeat the test.

Since an excess of CO_2 is liable to form the soluble acid calcium carbonate (see page 95), the formation of a precipitate should be looked for shortly after the bubbles begin to pass through the "lime water," as otherwise a precipitate might be formed and dissolved again without being noted.

In the presence of sulfurous acid, carbonic acid may escape detection since the volatile anhydrid, SO_2, will pass off with the CO_2. If SO_2 is present in large quantity, it may neutralize the lime water and even make the solution acid before CO_2 sufficient to produce a precipitate is liberated. If the odor of SO_2 is apparent while making this test and no indication of carbonic acid is noted, it will be safest to repeat the test on a fresh portion of the solution. Iodin water is added to the acidified solution until the color becomes permanent, thus indicating that all H_2SO_3 has been oxidized to H_2SO_4. The excess of iodin is bleached with a drop of $SnCl_2$ and the solution is then heated to drive the CO_2 into the "lime water."

TEST FOR OXALIC ACID.

Faintly acidify a portion of the *prepared solution* with acetic acid, warm and add an equal volume of a saturated solution of $CaSO_4$.

A white precipitate, **CaC_2O_4**, indicates the presence of **$H_2C_2O_4$**.

To confirm filter and wash the precipitate, dissolve in warm dilute H_2SO_4 and add a drop of a dilute solution of $KMnO_4$.

Bleaching of the permanganate confirms the test for **$H_2C_2O_4$**.

TESTS FOR TARTARIC ACID.

(1) Acidify a small portion of the aqueous solution with HCl and evaporate to dryness. (If the original substance is not soluble in water, use the HCl extract.) Ignite the residue thus obtained, noting carbonization or its absence.

Charring denotes the presence of non-volatile organic matter which *may be* tartaric acid. Absence of carbonization indicates the absence of **$H_2(C_4H_4O_6)$**.

(2) If the original substance contains carbonizing matter, to 10 ccm. of the *prepared solution* add a few granules of dry K_2CO_3 or sufficient to make the solution alkaline (Na_2CO_3 will not do). Evaporate until solid particles begin to separate. Dissolve the crystals in as little water as possible and acidify slightly with acetic acid. Add an equal volume of alcohol to the solution or as much less as is sufficient to cause incipient precipitation. Stand aside for 15 to 20 minutes. Filter off the precipitate, wash with a little ether* and dry thoroughly. Remove from filter and treat in a test-tube with $AgNO_3$ and sufficient NH_4OH to dissolve the precipitate. Place the test-tube in a beaker of boiling water and thus evaporate to dryness.

The formation of a silver mirror indicates the presence of **$H_2(C_4H_4O_6)$**.

(3) Acidify 10 ccm. of the *prepared solution* with HCl and boil thoroughly. Into the hot solution pass H_2S as long as any action takes place, add $BaCl_2$ and filter. Make the filtrate distinctly alkaline with Na_2CO_3, boil thoroughly and filter. Make filtrate slightly acid with acetic acid and boil, then add $CaCl_2$ and stand aside for 5–10 minutes, then filter. Make filtrate just alkaline with NH_4OH. White precipitate may indicate tartaric acid. Confirm by filtering and drying the precipitate, treating with $AgNO_3$ and NH_4OH and evaporating to dryness in boiling water as in Test (2).

The formation of a silver mirror indicates **$H_2(C_4H_4O_6)$**.

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* Ether must not be used in the vicinity of any flame.

DISCUSSION OF THE TEST FOR OXALIC ACID.

If the solution be free from $\overset{++}{Ba}$, $\overset{++}{Sr}$, and $\overset{++}{Pb}$ ions (as will be the case if the solution prepared for the Acid Analysis be used), nothing will interfere with this test for oxalic acid, since no other salts of calcium which are more insoluble than the sulfate will be precipitated in the presence of acetic acid. Since oxalic acid is easily oxidized, the presence of oxidizing agents in solution along with it might destroy it before it is precipitated as the calcium salt.

DISCUSSION OF THE TESTS FOR TARTARIC ACID.

The first test merely indicates the presence of some form of non-volatile organic matter. It is of value only as affording evidence as to whether it is necessary to make the more elaborate tests since, in the absence of carbonization, tartaric acid cannot be present.

Test (2) effects the separation of tartaric acid from other acids by precipitating it as acid potassium tartrate which is less soluble than any other salt of the alkali metals with the exception of potassium silicofluorid. Metals other than the alkalis must be absent, for they form tartrates more insoluble than the acid potassium salt. These have already been removed in making the prepared solution. The presence of $\overset{+}{K}$ ions is insured by the addition of K_2CO_3 and an equal volume of alcohol is added to the solution since $KH(C_4H_4O_6)$ is much less soluble in 50 per cent. alcohol than in water. The formation of a precipitate does not necessarily indicate tartaric acid but, if this acid is present, it will be contained in the precipitate and may be detected by the reduction of $AgNO_3$. Since alcohol may cause this same reduction it is necessary to remove it by washing with ether. In the presence of a slight amount of NH_4OH, silver salts are readily reduced to the metal by organic matter. Tartaric acid accomplishes this reduction on warming and deposits the silver as a brilliant mirror on the sides of the test-tube. (For further discussion see pages 86 and 125.)

Test (3) depends upon the precipitation of tartaric acid as the calcium salt and the subsequent reduction of $AgNO_3$ as confirmatory evidence. Inasmuch as many acids (Groups C, D, E; see page 276) are precipitated by the calcium ion, most of these must be removed, especially those which will react with $AgNO_3$ or reduce it to the metal. Thorough boiling with HCl decomposes and removes H_2SO_3 and $H_2S_2O_3$; H_2S removes the arsenic acids completely and reduces dichromic acid to the basic condition and $BaCl_2$ precipitates H_2SO_4 and H_2SiF_6. By boiling the filtrate with [illegible]$_2CO_3$, chromium and the excess of barium are precipitated and filtered off. The filtrate is acidified with acetic acid and boiled to remove H_2S and CO_2. The addition of $CaCl_2$ to the solution, which should be but faintly acid with $H(C_2H_3O_2)$, precipitates oxalic and hydrofluoric acids and after filtering and making alkaline with NH_4OH, tartaric acid is precipitated as the calcium salt. Certain other acids may be present in the precipitate, hence the indication should be confirmed by the formation of a mirror as outlined in Test (2).

TESTS FOR PHOSPHORIC ACID.

(1) Boil some of the *prepared solution,* or dry substance, with conc. HNO_3 as long as brown fumes (denoting oxidation) are given off, adding more acid, if necessary, to complete the reaction. Evaporate to dryness, and extract the residue by boiling with dil. HNO_3. Filter, if necessary, and add a drop or two of this solution to 5 ccm. of ammonium molybdate, $(NH_4)_2MoO_4$.

A yellow precipitate, $(NH_4)_3PO_4.12MoO_3$, indicates H_3PO_4 (*in the absence of* H_3AsO_4).

(2) If arsenic was indicated in the Basic Analysis, strongly acidify a portion of the *prepared solution* with HCl, heat to boiling and pass H_2S as long as a precipitate falls. Filter, boil out H_2S and treat as in Test (1).

A yellow precipitate, $(NH_4)_3PO_4.12MoO_3$, indicates H_3PO_4.

DISCUSSION OF THE TESTS FOR PHOSPHORIC ACID.

The formation of a yellow precipitate, $(NH_4)_3PO_4.12MoO_3$, with ammonium molybdate (see page 156), is a reaction characteristic of the ortho-phosphoric acid, but not of any other acid of phosphorus. The presence of any reducing agent interferes with the reaction by causing a reduction of the molybdate, which is indicated by the appearance of a blue color. It is therefore necessary to evaporate to dryness with conc. HNO_3 in order to destroy all reducing agents and oxidize any lower acids of phosphorus. The extraction with dilute HNO_3 causes the hydration of meta- and pyro-phosphoric acid. Thus, by this preliminary treatment all of the phosphorus is changed to ortho-phosphoric acid.

Arsenic acid with ammonium molybdate gives a precipitate closely resembling that with phosphoric acid (see page 164). The precipitate due to H_3PO_4 will come down in the cold solution after a few minutes' standing; but with H_3AsO_4 the precipitate cannot be brought down without warming, except on long standing. This difference is hardly sufficient to differentiate clearly; hence arsenic acid, if present, must be removed from solution before preparing for the phosphoric acid test.

Arsenic present in a form other than H_3AsO_4 will not give the reaction with molybdate; hence it might be thought that this would not interfere with the test. But under the treatment prescribed for obtaining phosphorus in the form of ortho-phosphoric acid, arsenic originally present in any form would be oxidized to arsenic acid. Hence, if arsenic is indicated in the Basic Analysis, it must be removed as in Test 2 before preparing for the test for H_3PO_4. Arsenic present in any form is precipitated as sulfid by this treatment. (For further discussion see page 261.)

TEST FOR ARSENIC ACID.

Boil a portion of the *original solution* with Na_2CO_3 to precipitate the base as in making the *prepared solution*, and filter. Acidify the filtrate to break up any carbonate and neutralize any fixed alkali, boil to remove CO_2, make alkaline with NH_4OH and add NH_4Cl and $MgCl_2$.

The formation of a white precipitate, $Mg(NH_4)AsO_4$, indicates H_3AsO_4 (*in the absence of H_3PO_4 and H_2SiO_3*).

To confirm, filter off the precipitate and wash with dilute NH_4OH. Moisten the precipitate with a few drops of $AgNO_3$.

The appearance of a chocolate color, Ag_3AsO_4, shown at once or on the addition of a drop of acetic acid, indicates H_3AsO_4.

TEST FOR ARSENIOUS ACID.

From the solution especially prepared as directed under the test for arsenic acid (see previous test) remove H_3AsO_4 by precipitation as $Mg(NH_4)AsO_4$ and filter. Evaporate the filtrate nearly to dryness and dissolve in 3–5 ccm. of conc. HCl. Add 3–5 drops of a conc. solution of $SnCl_2$ in conc. HCl.

The appearance of a dark brown precipitate, metallic **As**, indicates $\mathbf{H_3AsO_3}$.

DISCUSSION OF THE TEST FOR ARSENIC ACID.

The test for the acids of arsenic must be made on a portion of the *original solution* especially prepared, for from the regularly *prepared solution* all arsenic has been precipitated by H_2S.

Since all the salts of magnesium except the arsenate and phosphate (when formed under the conditions of this experiment) are soluble, nothing is likely to interfere with this test. The ammonium magnesium arsenate and phosphate resemble each other so closely as to be indistinguishable to the eye, and the differentiation has to be made on the basis of the transformation into the silver salt, which with arsenic is chocolate brown, with phosphorus pale yellow.

Silver arsenate, Ag_3AsO_4 is readily soluble in ammonium hydroxid, hence, after washing with NH_4OH, it may be necessary to neutralize with a drop of acetic acid to bring out the color.

If the prepared solution is yellow, indicating probably the presence of chromates, care must be taken to wash the precipitated $Mg(NH_4)AsO_4$ very thoroughly with NH_4OH until every trace of yellow color has been removed, for, with the chromate ion, the $\overset{+}{Ag}$ ion gives a deep red precipitate which might be confused with the chocolate-colored precipitate due to arsenic acid. A safer method would be to dissolve the precipitated magnesium salt on the filter paper with very dilute HNO_3 and wash into a test-tube. Then, by addition of dilute NH_4OH, it may be reprecipitated with little danger of inclusion.

Dilute NH_4OH is used to wash the precipitate, since the $Mg(NH_4)AsO_4$ is less soluble in it than in pure water.

It might appear that by direct addition of $AgNO_3$ to a neutral solution H_3AsO_4 might be indicated by the chocolate-colored precipitate at once without the necessity of separating it as the ammonium magnesium salt. Arsenic acid is far less frequently met with in analysis than most other inorganic acids, many of which give precipitates with the silver ion in neutral solutions (if not in the presence of HNO_3). Since Ag_3AsO_4 is more soluble than the silver salts of many other acids, H_3AsO_4 would not fall until after the other acids had been removed from the solution by precipitation; thus the test would be confused.

If soluble silicates are present, free silicic acid may be precipitated on the addition of NH_4Cl to the solution. This precipitate is due to hydrolysis of the ammonium silicate formed by metathesis (see page 135), but its gelatinous character generally serves to differentiate it from the crystalline $Mg(NH_4)AsO_4$.

DISCUSSION OF THE TEST FOR ARSENIOUS ACID.

Since the solution prepared for this test is free from all metals except arsenic and antimony, nothing is likely to interfere with this test, since none of the compounds of antimony will give a similar precipitate with $SnCl_2$.

If arsenic exists in the prepared solution, and be not present in the form of arsenic acid (which will be removed as $Mg(NH_4)AsO_4$), it will be present as arsenious acid or its equivalent.

It is necessary that the trivalent arsenic should exist in the solution as arsenic chlorid, *i. e.*, acting the part of a metallic element, and not as arsenious acid. Hence it is absolutely necessary that the test be conducted in the presence of conc. HCl. (See discussion of AsO_3H_3, page 159.)

TEST FOR SULFUROUS ACID.

Acidify a portion of the *prepared solution* with acetic acid and add zinc acetate, $Zn(C_2H_3O_2)_2$, as long as a precipitate falls. Filter off the precipitate[*] and test the filtrate with a drop of $Zn(C_2H_3O_2)_2$ to see that precipitation is complete. (Should a precipitate fall, add more zinc acetate solution and filter again.) To the filtrate add $BaCl_2$ in considerable excess and filter until a clear solution is obtained.[†] To the clear filtrate add iodin water until color becomes permanent, then a little *conc.* HCl and bleach with a *drop or two* of $SnCl_2$.

White precipitate, **$BaSO_4$**, indicates **H_2SO_3**.

[*] This precipitate may be tested for H_2S by treating with H_2SO_4, warming and exposing a filter paper moistened with lead acetate solution to the action of the fumes evolved. A black stain, **PbS**, indicates the presence of **H_2S**.

[†] The precipitate obtained here may be dried and tested for H_2SO_4 by heating before the blowpipe with Na_2CO_3 on charcoal. Remove the melt, place on a silver coin and moisten with a drop of water. A black stain, **Ag_2S**, indicates the presence of **H_2SO_4**.

TEST FOR THIOSULFURIC ACID.

Acidify a portion of the *prepared solution* with acetic acid and add zinc acetate, $Zn(C_2H_3O_2)_2$, as long as a precipitate falls. Filter off the precipitate and test the filtrate with a drop of $Zn(C_2H_3O_2)_2$ to see that precipitation is complete. (Should a precipitate fall, add more zinc acetate solution and filter again.) To the filtrate add $BaCl_2$ in considerable excess and filter until a clear solution is obtained. To the clear filtrate add iodin water until color becomes permanent, then a little *conc.* HCl and bleach with a *drop or two* of $SnCl_2$.[‡] Filter (if necessary) until the filtrate becomes clear, add bromin water until the solution becomes permanently colored and bleach with a drop or two of $SnCl_2$.

White precipitate, **$BaSO_4$**, indicates presence of **$H_2S_2O_3$** (*in the absence of HSCN*).

[‡] The directions for making the test for thiosulfuric acid up to this point are identical with the test for sulfurous acid (see above). Time may be saved, therefore, by testing for thiosulfuric acid immediately after testing for sulfurous acid by adding bromin water to the solution (filtered clear, if necessary) that was used in testing for sulfurous acid and proceeding as directed.

DISCUSSION OF THE TEST FOR SULFUROUS ACID.

The test for sulfurous acid depends upon its oxidation by iodin to sulfuric acid (see page 185) and its subsequent precipitation as the barium salt. To prevent a similar oxidation, H_2S (if present) is removed as ZnS and any H_2SO_4 already present is precipitated as $BaSO_4$. If on the addition of iodin water to the solution thus prepared a second precipitation of $BaSO_4$ falls, it must be due to H_2SO_3, for this compound *only* is oxidized to H_2SO_4 by iodin.

Nothing will interfere with this test except the presence of oxidizing agents which will act on sulfurous acid as soon as the solution is acidified. Of these dichromic acid will be precipitated as $BaCrO_4$ along with H_2SO_4 and thus removed in the preliminary treatment. Of the other common oxidizing acids (see page 276) the barium salts are all soluble and may be separated from the sulfite which is insoluble. To the neutral or slightly alkaline solution $BaCl_2$ is added as long as precipitation follows. This precipitate, which will contain among other salts $BaSO_3$, is filtered off and treated with HCl when the sulfite dissolves and may be tested for in the solution as directed.

Bleaching of the solution with $SnCl_2$ (see page 138) renders a slight precipitate more plainly visible. It may be omitted if the precipitate is evident.

By testing the precipitate brought down by zinc acetate for H_2S and the first precipitate by $BaCl_2$ (before the addition of iodin water) for H_2SO_4 (as directed in the footnotes on the opposite page), these acids may be detected also. If thiosulfuric acid is tested for in the same solution (see next test), all of the four sulfur acids, H_2S, H_2SO_4, H_2SO_3 and $H_2S_2O_3$, may be detected in the presence of each other.

DISCUSSION OF THE TEST FOR THIOSULFURIC ACID.

This test depends upon the fact that, when treated with iodin, thiosulfuric acid is oxidized only to tetrathionic acid, the barium salt of which is soluble.

$$2H_2S_2O_3 + 2I \rightarrow H_2S_4O_6 + 2HI$$

The stronger action of bromin, however, oxidizes tetrathionic acid to sulfuric acid (see page 189) and in the presence of the barium ion a precipitate of $BaSO_4$ is obtained which in this case indicates $H_2S_2O_3$.

After the removal of other sulfur acids (see discussion of the previous test) nothing will interfere with the detection of thiosulfuric acid except the presence of oxidizing agents and of thiocyanic acid. The former may be separated exactly as indicated in the discussion of the test for sulfurous acid; for barium thiosulfate, like barium sulfite, is quite insoluble in water.

Thiocyanic acid, if present, will be oxidized to H_2SO_4 by bromin and, hence, must be removed. This is most satisfactorily accomplished before beginning the test for sulfurous acid by *faintly* acidifying the solution with HNO_3 and adding $AgNO_3$ as long as a precipitate, $AgSCN$ and possibly other salts, falls. The filtrate is made slightly alkaline with $NaOH$ and again filtered, after which the regular treatment for H_2SO_3 and $H_2S_2O_3$ is to be followed.

TEST FOR FERROCYANIC ACID.

Acidify a portion of the *prepared solution* with HCl and add a drop of $FeCl_3$ solution.

A deep blue color, $\mathbf{Fe_4(Fe=C_6N_6)_3}$, indicates $\mathbf{H_4(Fe=C_6N_6)}$.

TEST FOR FERRICYANIC ACID.

Acidify a portion of the *prepared solution* with HCl and add to it a few drops of a *freshly prepared* solution of $FeSO_4$.

A *dark blue* precipitate, $\mathbf{Fe_3(Fe\equiv C_6N_6)_2}$, indicates $\mathbf{H_3(Fe\equiv C_6N_6)}$.

TESTS FOR THIOCYANIC ACID.

(1) Acidify a portion of the *prepared solution* with HCl and add $\mathbf{FeCl_3}$.

A deep red color, $Fe(SCN)_3$, bleached by the addition of $HgCl_2$, indicates **HSCN.**

(2) Acidify a portion of the *prepared solution* with HCl; add $SnCl_2$, if necessary, to hold back iodin or bromin which may be liberated and by the color produced interfere with the test to follow. Boil, collecting the volatile thiocyanic acid in a trap containing $FeCl_3$.

The formation of a red color due to $Fe(SCN)_3$ indicates **HSCN.**

DISCUSSION OF THE TEST FOR FERROCYANIC ACID.

Because of the intensity of the color produced, nothing is likely to interfere with this test. When only a small amount of ferrocyanic acid is present in a solution, the deep blue precipitate may be so sparsely diffused as to produce a green rather than a blue color, especially if the solution be colored yellow by an excess of ferric chlorid present. Under these circumstances, if the indication is doubtful, it is best to pour the solution into a test-tube and allow the precipitate to settle, when its deep blue characteristic appearance will sufficiently indicate its nature.

DISCUSSION OF THE TEST FOR FERRICYANIC ACID.

Nothing is likely to interfere with the successful working of this reaction unless the presence of oxidizing agents should carry the iron from the ferrous to the ferric condition. Under these circumstances it is better to reduce oxidizing agents with sodium sulfite in acid solution. In an acid solution a ferricyanid is not appreciably reduced to a ferrocyanid.

Ferrous salts oxidize so quickly in the air that it is essential that a fresh solution be made for each test by shaking a crystal of $FeSO_4$ with a few cubic centimeters of water. An intense dark blue color, appearing immediately, alone indicates the presence of ferricyanic acid; for, if ferrocyanic acid is present, under the conditions of the experiment a light blue precipitate will form which will grow visibly darker in a few moments, the deepening of the color, and the oxidation of the ferrous salts causing it, being hastened by vigorous shaking or pouring the solution through the air.

DISCUSSION OF THE TESTS FOR THIOCYANIC ACID.

In a neutral solution acetic acid would interfere with Test (1) by the production of a red color due to ferric acetate. Under the same conditions tartaric acid and similar hydroxy acids tend to form complex compounds which remove ferric ions from solution. In an acid solution none of these substances interfere.

Iodids, if present, may interfere with the test for traces of thiocyanic acid in the way already indicated (see page 283). If oxidizing agents by present in solution, iodin may be set free in quantity when the solution is made acid, and therefore may interfere decidedly. This interfering action may be avoided by carefully bleaching out the solution with stannous chlorid, avoiding an excess, since the stannous ion will reduce ferric salts to the ferrous condition and thus require a large amount of ferric chlorid to bring out the red color due to thiocyanic acid.

If ferrocyanic or ferricyanic acids be present in the solution, the deep blue color due to these reagents may completely mask the red color due to thiocyanic acid. Under these circumstances it is best to distil out thiocyanic acid as directed in Test (2).

TESTS FOR HYDROCYANIC ACID.

(1) Make a portion of the *prepared solution* alkaline with NaOH, add a few drops of $FeSO_4$ solution and boil. Add a single drop of $FeCl_3$ and acidify with HCl.

A deep blue color, $\mathbf{Fe_4(Fe=C_6N_6)_3}$, indicates **HCN.**

(2) Add to a portion of the *prepared solution* a drop or two of yellow ammonium sulfid and boil for a few minutes. Cool, acidify with HCl and add $FeCl_3$.

A red color, $Fe(SCN)_3$, indicates **HCN.**

(3) Make a portion of the *prepared solution* alkaline with NaOH and add a drop of a dilute solution of mercurous nitrate, $(HgNO_3)_2$. A black precipitate of mercurous oxid, Hg_2O, will form.

If, on shaking, the black precipitate disappears and a gray one, due to metallic **Hg**, appears in its place, it is an indication of the presence of **HCN.**

TESTS FOR HYDROSULFURIC ACID.

(1) Treat a portion of the dry substance, or the *prepared solution,* with HCl and heat, allowing the fumes to come in contact with a filter paper moistened with $Pb(C_2H_3O_2)_2$.

A black stain, **PbS**, indicates $\mathbf{H_2S}$.

(2) If no black stain appears in (1) and the original substance remains undissolved, fuse it with NaOH on a crucible cover. Place the melt on a silver coin and moisten with a few drops of water.

A black stain, $\mathbf{Ag_2S}$, indicates $\mathbf{H_2S}$.

DISCUSSION OF THE TESTS FOR HYDROCYANIC ACID.

Since Test (1) depends upon the transformation of the simple cyanid ion, $\overline{C}N$, into the complex ferrocyanid ion, $(Fe = \overset{=}{C}_6N_6)$, if ferrocyanids be present in the original solution, the result of the test is obviously worthless. Ferricyanic acid gives a deep blue color with ferrous salts, hence, if present, it will interfere with the test. Furthermore, if thiocyanic acid in considerable amount and traces only of hydrocyanic acid are present, the intense red color due to the former will probably mask the slight blue tint due to the latter, so that tests cannot be made satisfactorily on the solution. For similar reasons, the second method is no more satisfactory than the first under these circumstances.

Advantage is taken, therefore, of the weak acidic properties of HCN to separate it from the other stronger cyanogen acids which may be present. The solution is made exactly neutral with HCl or NaOH, and dry acid sodium carbonate, $NaHCO_3$, is added to it. Since carbonic acid is stronger than hydrocyanic acid, but weaker than ferro-, ferri, or thiocyanic acids, HCN alone will be set free under these conditions. On gently warming the solution HCN may be distilled out and collected in a trap containing a little water. More satisfactory results can be obtained by distilling in an atmosphere of carbon dioxid.

Test (2) depends upon the oxidation of HCN to HSCN by the free sulfur contained in the solution of yellow ammonium sulfid. (See page 126.)

Since hydriodic acid is oxidized slowly by ferric salts with the liberation of free iodin, a slight color due to this reaction may develop on standing if iodids are present. It is not likely to interfere seriously, however, as the action of ferric chlorid would take place in slight degree only.

Test (3) depends on the reduction of mercurous oxid to the metal through the agency of the cyanid, as the following equations indicate:

$$Hg_2O + 2NaCN + H_2O \rightarrow (HgCN)_2 + 2NaOH$$

$$(HgCN)_2 \rightarrow Hg(CN)_2 + Hg$$

DISCUSSION OF THE TESTS FOR HYDROSULFURIC ACID.

Certain sulfids are not readily decomposed by HCl and therefore do not respond satisfactorily to Test (1). When fused with NaOH, all sulfids are transposed and to a large extent oxidized to sulfates. Sufficient unoxidized Na_2S will be present, however, to produce a stain on silver due to the formation of Ag_2S. Oxygen is absorbed during the reaction according to the equation:

$$\mathbf{4Ag} + 2Na_2S + O_2 + 2H_2O \rightarrow \mathbf{2Ag_2S} + 4NaOH$$

TESTS FOR HYDRIODIC ACID.

(1) Acidify a portion of the prepared solution with HNO_3, **add one to**
ccm. of CS_2 and treat with chlorin water, or if reducing **agents are present,**
$K_2Cr_2O_7$, shaking the mixture vigorously after each **addition of the**
The appearance of a purple color in the CS_2 due to **free iodin indicate**

(2) Acidify a portion of the *prepared solution* with HNO_3, **add**
and boil.

The evolution of purple fumes of iodin producing blue color on **a filter**
moistened with starch paste indicates **HI.**

DISCUSSION OF THE TESTS FOR HYDRIODIC ACID.

Although chlorin water will liberate both bromin and iodin from their respective acids (see page 200), it is to be preferred to bromin water, which liberates only iodin (see page 208), since chlorin does not color CS_2. Since all iodin is liberated before any bromin is set free, with careful manipulation no confusion will result even if the solution contains only traces of iodid in the presence of much bromid.

Care must be taken to avoid the addition of a large amount of chlorin water *at the start* since an excess of chlorin will unite with free iodin to form colorless iodin chlorid (see page 211), which will not affect the CS_2. Hence a few drops of chlorin water should be added at first, followed by larger amounts later if an indication does not appear. The mixture should be thoroughly shaken after each addition.

Certain reducing agents, such as H_2S, H_2SO_3, $H_2S_2O_3$, HNO_2 especially, are so easily oxidized that the chlorin is entirely absorbed by them before it can set free iodin from hydriodic acid. If they be present in the solution in relatively large proportion there may be no indication of HI even after the repeated addition of the necessarily dilute reagent, chlorin water. If these acids are suspected or known to be present, the test may be more satisfactorily performed by the use of $K_2Cr_2O_7$ which will evidence by change of color from yellow to green that it is being reduced. Sufficient dichromate is added to cause the appearance of a yellow tint in the solution, thus indicating an excess of the reagent.

Nitrous acid is somewhat soluble in CS_2 forming a red-colored solution. If nitrites be present when Test (1) for HI is made, the CS_2 will take on a color which might be confused with the purple tint produced by iodin. Since iodin is six hundred times more soluble in CS_2 than in water, the color due to iodin cannot be removed by shaking with water. Nitrous acid is about as readily soluble in one as the other, however, and the color due to it can be removed by pouring off the solution from which it was extracted, washing by decantation and shaking vigorously with a test-tube of water. Under these conditions nitrous acid for the most part passes into the water and the color leaves the CS_2.

TESTS FOR HYDROBROMIC ACID.

(1) To a portion of the *prepared solution* acidified with HNO_3 add 1-2 ccm. of CS_2. Treat with chlorin water and shake mixture thoroughly.

The appearance of a color in the CS_2, red or yellow according to the concentration of the free bromin present, indicates **HBr.**

(2) Acidify a portion of the *prepared solution* with HNO_3 and add $KMnO_4$ until the solution is colored red permanently. Heat to boiling and collect the volatilized bromin in a trap containing chloroform.

A reddish-brown color indicates **HBr.**

TESTS FOR HYDROCHLORIC ACID.

(1) Acidify a portion of the *prepared solution* with HNO_3 and add $AgNO_3$.

The formation of a curdy white precipitate, **AgCl** (readily soluble in NH_4OH, reprecipitated on the addition of HNO_3, darkening in the sunlight), indicates **HCl** (*in the absence of HCN and HSCN*).

(2)* Evaporate some of the *prepared solution* to dryness, add solid $K_2Cr_2O_7$ and 5 ccm. conc. H_2SO_4, passing the fumes through a trap containing a drop or two of water. Rinse out the trap into a test-tube, heat to boiling if necessary to remove free bromin and iodin and add a grain or two of Na_2O_2.

The appearance of a transient blue color, $HCrO_4$, at once or on acidifying with H_2SO_4, denotes the presence of **HCl.**

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* In the presence of chlorates Test (2) is prohibited owing to the explosive character of the mixture of chlorates and conc. H_2SO_4. In order to avoid danger Test (1) for $HClO_3$ (see page 304) should be made before making this test for HCl. If chlorates are indicated, the separation of chlorids may be effected by acidifying a portion of the prepared solution with HNO_3 and adding $AgNO_3$ as long as a precipitate falls. The filtered and washed precipitate is transferred to a small porcelain crucible, covered with dilute H_2SO_4 and a piece of Zn laid upon it. After 15–30 minutes, the metathesis represented by the following equation will have taken place and the decanted solution may be evaporated to dryness and tested for HCl as in (2).

$$2AgCl + Zn \rightarrow ZnCl_2 + 2Ag$$

DISCUSSION OF THE TESTS FOR HYDROBROMIC ACID.

Since chlorin water liberates both bromin and iodin, Test (1) cannot be used satisfactorily when both HBr and HI are present, since iodin is liberated first and colors the CS_2 purple. Under these circumstances permanganate offers a satisfactory differentiation, since HBr is oxidized to water and free bromin which may be boiled off while non-volatile iodic acid, HIO_3 (see page 211) is formed from HI. Care should be taken not to boil the solution too vigorously lest the heat from the steam vaporize the chloroform—boiling-point 61.5°.

DISCUSSION OF THE TESTS FOR HYDROCHLORIC ACID.

Under the conditions of the experiment, HCl, HBr and HI are all oxidized to water and the free halogen. Iodin and bromin are volatilized but chlorin unites with the chromic acid anhydrid, CrO_3, formed by the dehydrating action of conc. H_2SO_4 on $K_2Cr_2O_7$, to produce chloro-chromic anhydrid, CrO_2Cl_2 (see page 196). Since the latter compound boils at 116° it is necessary to heat quite strongly to drive it into the trap where it reacts with water to form HCl and $H_2Cr_2O_7$. Inasmuch as $H_2Cr_2O_7$ is more readily detected than HCl under the conditions of the experiment, generally the former is tested for by Na_2O_2 and its presence considered as indicating the presence of the latter also. Care should be taken to prevent the liquid in the test-tube from being carried mechanically into the trap by spattering, as this would give a test not due to the volatilized CrO_2Cl_2.

If it is necessary to make tests for HCl, HBr and HI from the same portion of solution, the use of chlorin or bromin water has to be avoided since these reagents introduce into the solution two of the acids to be tested for. It is necessary, therefore, to detect HI according to the second test as given under hydriodic acid, then HBr according to the second test for hydrobromic acid and finally HCl from the resulting solution evaporated to dryness.

TESTS FOR NITRIC ACID.

(1) Saturate a portion of the water extract of the original substance $FeSO_4$ and pour conc. H_2SO_4 down the side of the inclined test-tube in suc manner that the acid will underlie the solution.

The formation of a dark ring, due to $(FeSO_4)_2.NO$, on the line of separat of the two liquids indicates **HNO_3** (*in absence of HNO_2*).

(2) Acidify a portion of the *prepared solution* with H_2SO_4 and heat, ad KI drop by drop, to the boiling solution until all iodin and oxids of nitrogen driven off. Then make the solution strongly alkaline with NaOH and boil out NH_3 that may be present. Add a mixture of finely divided iron and zinc, little Devarda's alloy, and boil again.

The evolution of NH_3, recognized by its odor or action on red litmus, i cates the presence of **HNO_3**.

(3) Evaporate a portion of the *prepared solution* almost to dryness cool. Add three times its volume of conc. H_2SO_4 and a drop of the bru solution.

A red color, changing to yellow and possibly green, indicates **HNO_3** (*in absence of $HClO_3$*).

DISCUSSION OF THE TESTS FOR NITRIC ACID.

Test (1) serves for the detection of nitric acid in the presence of all other acids with the exceptions of nitrous acid (which gives the same test) and of the interfering substances noted below.

Test (2) removes HNO_2, the only other acid that will give the same reaction and, therefore, may be used to detect nitric acid in the presence of any other acids.

Test (3) will detect nitric acid in the presence of nitrous acid and of any others except chloric acid.

Iodids, bromids, ferrocyanids, ferricyanids and oxidizing agents in general interfere with Test (1). In contact with conc. H_2SO, hydrobromic and hydriodic acids are oxidized with the liberation of iodin and bromin which produce a similar coloration. The ferrocyanid and ferricyanid ions form blue precipitates with the ferrous ion, making the test very indefinite. Chromates, dichromates and permanganates interfere because of their color.

In solutions ordinarily met with in qualitative analysis ferrocyanids and ferricyanids, chromates, and permanganates are not likely to be present. In many kinds of work bromids and iodids occur very rarely. Hence the test is a valuable means of detecting the acids of nitrogen, one or both, and is the method most generally used. Although the interfering acids may be removed from solution, if present it is more satisfactory to use the other tests.

Test (1) depends upon the reduction of nitric (or nitrous) acid by means of ferrous sulfate and the interaction of the reduction product, NO, with the same reagent. (See page 151.)

Test (2) depends upon the fact that zinc and aluminum are acted upon by alkaline hydroxids, forming sodium zincate, Na_2ZnO_2, or sodium aluminate, Na_2AlO_2, and nascent hydrogen (see pages 102 and 115). The iron mixed with the zinc, or the copper in the alloy forms an electrolytic couple within the solution and aids the reaction. Nascent hydrogen acting on nitric acid under these conditions reduces it to ammonia. The presence of other oxidizing agents may delay but cannot prevent the formation of ammonia.

Although nitrous acid reacts readily with hydriodic acid and is rapidly destroyed (see page 211) as in Test (2), some small part usually decomposes into nitric acid and nitrogen dioxid according to the regular reaction in water solution (see page 148). Hence in solutions containing nitrous acid only, traces of nitric acid are frequently indicated. If to the neutral or alkaline solution to be tested a relatively large amount of conc. H_2SO_4 is added, this formation of nitric acid does not take place. Brucin does not respond to nitrous acid and since the formation of nitric from nitrous acid is prevented, Test (3) becomes the method of last resort for the detection of nitric acid in the presence of nitrous acid.

TESTS FOR NITROUS ACID.

(1) Saturate a portion of the water extract of the original substance $FeSO_4$ and make slightly acid with acetic acid.

A dark brown color, $(FeSO_4)_2.NO$, indicates HNO_2.

(2) Acidify a portion of the *prepared solution* and add a few drops phenylenediamin in HCl solution.

A yellow color indicates HNO_2.

(3) Make a portion of the *prepared solution* neutral and add 1 ccm. of sulfanilic acid mixture.

A red color indicates HNO_2.

TESTS FOR ACETIC ACID.

(1) Treat some of the dry substance with 1–2 ccm. of the ordinary e alcohol, or with amyl alcohol, and 5 ccm. of conc. H_2SO_4 and warm (not h The evolution of the characteristic ethereal odor indicates $H(C_2H_3O_2)$.

(2) To the neutral solution to be tested add $FeCl_3$.

The appearance of a deep red color strongly indicates acetic acid, the p ence of which may be confirmed by diluting the solution abundantly and boil

A red precipitate, $Fe(C_2H_3O_2)(OH)_2$, indicates $H(C_2H_3O_2)$.

DISCUSSION OF TESTS FOR NITROUS ACID.

Test (1) for nitrous acid is very similar to Test (1) for nitric acid (see page 300), the difference being only in the strength of the acid used to acidify the solution. Nitrous acid is weaker than acetic acid, hence is liberated by it and reacts characteristically. Nitric acid, which reacts similarly to nitrous acid (see pages 149 and 151), is much stronger than acetic acid, hence is not set free. With acetic acid, therefore, the dark color indicates HNO_2 alone; but when sulfuric acid is used, HNO_3 as well as HNO_2 is set free and the color may be due to either. With the exception of HBr (which is not oxidized by HNO_2) the same substances that interfere with Test (1) for nitric acid hinder this test for nitrous acid also.

The colors developed in Tests (2) and (3) are due to characteristic reactions of nitrous acid (see page 149). Nothing will interfere with these reactions. Should an indefinite indication be obtained because of very dilute solutions, it may be advisable to make a blank test to make sure of the indication. Acidify about 20 ccm. of water with HCl, add a few drops of the reagent solution and divide equally between two test-tubes. To one add the solution to be tested. The development of a tint in the test-tube to which the unknown solution was added indicates the presence of nitrous acid in it.

DISCUSSION OF TESTS FOR ACETIC ACID.

Test (1) depends upon the formation of ethyl or amyl acetate by the union of acetic acid with the corresponding alcohol. Alcohols are organic bases—hydroxids—and in the reaction with acids water is set free just as with inorganic bases.

$$\underset{\text{ethyl alcohol}}{(C_2H_5)OH} + H(C_2H_3O_2) \rightarrow \underset{\text{ethyl acetate}}{(C_2H_5)(C_2H_3O_2)} + H_2O$$

$$\underset{\text{amyl alcohol}}{(C_5H_{11})OH} + H(C_2H_3O_2) \rightarrow \underset{\text{amyl acetate}}{(C_5H_{11})(C_2H_3O_2)} + H_2O$$

Concentrated H_2SO_4 is added to liberate acetic acid from its salts and to unite with the water formed during the reaction and prevent reversal (see page 23).

It is necessary that the characteristic odor of ethyl and amyl acetates become familiar to the observer in order that he may differentiate it clearly from the odor of ethyl or amyl alcohol. If necessary a blank test may be made.

Test (2) depends upon the hydrolysis of ferric acetate in a solution slightly acid with acetic acid. In order to keep ferric salts in solution it is necessary to add a little free acid. When a ferric salt is added to a neutral solution of an acetate, therefore, the free acid present, usually HCl, liberates a little acetic acid and forms a corresponding amount of chlorid. The amount of free acid is therefore the determining factor in the success of this test. Care must be taken that the solution before the addition of the ferric salt is not alkaline but distinctly neutral. If alkaline, ferric hydroxid may be precipitated and furnish no indication at all of the presence of acetic acid. If the solution be acid ferric acetate may not be formed at all and so not give the red color to the solution. At any rate, if the solution is too acid, the precipitation of basic ferric acetate would be prevented.

Other organic acids, not included in this manual and rarely met with in analysis, when similarly treated, separate basic ferric salts indistinguishable from the basic acetate.

TESTS FOR CYANIC ACID.

(1) Neutralize a portion of the *prepared solution* and concentrate to a small bulk. Add 1 to 2 ccm. of a strong solution of cobalt acetate, $Co(C_2H_3O_2)_2$.

A blue coloration due to $K_2(CoO_4C_4N_4)$, appearing at once or on the addition of an equal volume of alcohol, indicates **HOCN** (*in the absence of HSCN*).

(2) If not already so, make a portion of the *prepared solution* alkaline with NaOH and boil until NH_3 (if present) is entirely removed. Cool, acidify the solution with H_2SO_4 and test the gas evolved for CO_2, liberated on acidifying a solution containing a cyanate. Boil until all H_2S (if any be present) has been driven off along with CO_2. Make the solution alkaline with NaOH and boil, testing the gas evolved with red litmus paper or mercurous nitrate on a filter paper.

The turning blue of the litmus paper or the production of a black stain with mercurous nitrate is due to NH_3 set free by the decomposition of **HOCN.**

TEST FOR HYPOCHLOROUS ACID.

Make a portion of the aqueous extract of the original substance strongly alkaline with Na_2CO_3 and add 3–5 drops of $H(C_2H_3O_2)$, shaking thoroughly after each drop. Care should be taken not to add acetic acid in sufficient quantity to produce a marked effervescence or to make the solution acid. Insert a piece of litmus paper.

Bleaching of the litmus indicates **HOCl** (*in the absence of* $HMnO_4$, which may be recognized by its color).

If HOCl is present, it may be recognized by the characteristic odor of this solution—like that of "bleaching salt."

TESTS FOR CHLORIC ACID.

(1) To a small portion of the dry substance (*caution!—use a few grains only*) add conc. H_2SO_4 and warm gently.

A slight explosion or crackling due to ClO_2 indicates **$HClO_3$**.

(2) Acidify a small portion of the *prepared solution* with HNO_3, heat to boiling and add $AgNO_3$ until precipitation ceases. Shake thoroughly to coagulate the precipitate, filter and to the clear filtrate add solid Na_2SO_3 until the odor of SO_2 is apparent.

A white precipitate, **AgCl** (insoluble in boiling water to which a little HNO_3 is added, but readily soluble in NH_4OH), indicates **$HClO_3$**.

DISCUSSION OF THE TESTS FOR CYANIC ACID.

Since the test with cobalt acetate (see page 128) is not given by cyanates in the presence of cyanids, these are removed (if present) by passing CO_2 through the neutral solution for from 15–90 minutes, the time necessary being dependent upon the amount of cyanid present. Under these conditions hydrocyanic acid is set free (see page 295) and swept from the solution by the carbon dioxid, while the cyanate is not appreciably affected.

Since thiocyanates give the test with cobalt acetate as well as the cyanates, in the presence of thiocyanates the indication is equivocal and resort must be had to the second test. Any ammonium salts present in solution will be broken up and removed on boiling the alkaline solution. On acidifying, the cyanate is decomposed into NH_3 which unites with the excess of acid and remains in solution, while CO_2 is driven off. Of course the presence of carbonates would liberate CO_2 so that its detection would not indicate the presence of cyanates except in the absence of carbonates. In any case it is better to confirm by testing for NH_3 on making the solution alkaline. Mercurous nitrate can be used with advantage to detect the presence of NH_3 (see page 110), since all H_2S (which also produces a black stain) should be removed by boiling the acid solution until it gives no stain on lead acetate paper.

DISCUSSION OF THE TEST FOR HYPOCHLOROUS ACID.

All hypochlorites are soluble and will therefore be found in the aqueous extract. Silver hypochlorite decomposes, however, into silver chlorid and chlorate (see page 205). Consequently, unless a precipitate is obtained with $AgNO_3$ in the preliminary testing for acids, hypochlorites are not present.

The test depends upon the fact that, HOCl being very weak, is set free from its salts by the carbonic acid liberated by the interaction of acetic acid and sodium carbonate, even though the solution is alkaline in reaction due to the presence of acid carbonates of the alkali metals (see page 204).

DISCUSSION OF THE TESTS FOR CHLORIC ACID.

Test (1) depends on the formation of ClO_2 which decomposes explosively into its elements. Chloric acid is at first set free and then breaks down, according to the equation:

$$3HClO_3 \rightarrow HClO_4 + H_2O + 2\mathit{ClO_2} \rightarrow \mathit{Cl_2} + 2\mathit{O_2}$$

Care must be taken to use only a few grains of the substance to be tested as serious explosions result from the interaction of chlorates and sulfuric acid in too large amounts.

Test (2) depends upon the reduction of $HClO_3$ to HCl by sulfurous acid. Chlorids and hypochlorites are removed from the solution by the addition of the $\overset{+}{Ag}$ ion in excess. After filtering, the sulfite is introduced. If a further precipitate of AgCl falls, it is due to $HClO_3$, for $HClO_4$ is not decomposed by ordinary reducing agents. White Ag_2SO_4 or Ag_2SO_3 may be precipitated from the concentrated solution, but either will dissolve readily when boiled with water containing a little HNO_3.

$AgNO_3$ if a precipitate has not already formed.

A white precipitate of **AgCl** (soluble in NH_4OH and darkening in indicates **$HClO_4$**.

* The directions for making the test for perchloric acid up to this identical with the test for chloric acid (see page 304). Time may be saved, by testing for perchloric acid immediately after testing for chloric aci tinuing the treatment as further directed.

TEST FOR PERMANGANIC ACID.

If the aqueous extract of the original substance is colored red, portion with H_2SO_4 and add Na_2SO_3.

Bleaching of the red color indicates the presence of **$HMnO_4$**.

TESTS FOR HYDROGEN PEROXID.

Treat a portion of the finely powdered substance with dil. H_2S gently and stand aside for 10–15 minutes, shaking vigorously from time. Filter clear and use the filtrate in making the following tests. original substance is already in solution, acidify a portion with H_2SO_4

DISCUSSION OF THE TEST FOR PERCHLORIC ACID.

After the decomposition of hypochlorites and chlorates into chlorids and the removal of the latter as AgCl, the solution can contain no other acid of chlorin than $HClO_4$. By evaporation and ignition of the resulting filtrate, the perchlorate is decomposed into the chlorid and oxygen. By the treatment with NaOH, any excess of $AgNO_3$ that is present will be precipitated as the hydroxid. This decomposes at once into the oxid and this on heating into metallic silver. By boiling with HNO_3, $AgNO_3$ will be formed again and a precipitate of AgCl under these circumstances will indicate $HClO_4$. If no precipitate is seen, it is safest to add a few drops of $AgNO_3$ to be certain that the $\overset{+}{\mathrm{Ag}}$ ion is present.

DISCUSSION OF THE TEST FOR PERMANGANIC ACID.

If permanganic acid is present during the Basic Analysis, it will be reduced by H_2S to the divalent basic condition and detected in Group III. If manganese is not detected in the Basic Analysis, it is unnecessary to test for the presence of $HMnO_4$ among the acids.

DISCUSSION OF THE TESTS FOR HYDROGEN PEROXID.

Of the commoner peroxids (salts of H_2O_2) Na_2O_2 and K_2O_2 are soluble in water. Others are more or less soluble in acids, but require careful treatment in order not to decompose the H_2O_2 formed. For this reason heating is to be avoided.

Test (1) depends on the oxidation of titanium from the tetravalent to the hexavalent condition which is characterized by the deep orange-red color.

Test (2) depends upon the interaction of hydrogen peroxid and ferricyanic acid by virtue of which both are reduced, the former to water, the latter to ferrocyanic acid. This last substance reacts with the ferric salt to produce Prussian blue. Oxygen is liberated by the interaction of H_2O_2 with $H_3(Fe \equiv C_6N_6)$ as the equation shows:

$$2H_3(Fe \equiv C_6N_6) + H_2O_2 \rightarrow 2H_4(Fe = C_6N_6) + O_2$$

Test (2) is obviously not applicable in the presence of ferrocyanic acid or of large amounts of thiocyanic acid.

deposited on the cooler parts of the test-tube indicates **H.**

(2) **Nitrogen.** Ignite a portion of the substance with a small p metallic sodium in a tube of hard glass. Drop the tube while still hot beaker containing 20 or 30 ccm. of water. Boil and filter. Add to the a small crystal of $FeSO_4$, and a drop of $FeCl_3$. Boil for a few minu acidify.

A deep blue color, $\mathbf{Fe_4(Fe=C_6N_6)_3}$, indicates **N.**

(3) **Sulfur.** Ignite a portion of the substance with metallic sodiur (2). Boil out with water, filter and divide the solution.

(*a*) Into one portion drop a bright silver coin and allow to stand fo time.

Light brown stain of $\mathbf{Ag_2S}$ indicates the presence of **S.**

(*b*) To the second portion add a few drops of a solution of sodium ferricyanid, $Na_2Fe(CN)_5NO$.

A purple color indicates **S.**

(*c*) Slightly acidify a third portion with $H(C_2H_3O_2)$ and add Pb(C

Black precipitate, **PbS,** indicates **S.**

(4) **Chlorin, Bromin and Iodin.** Ignite a portion of the substanc test-tube with lime. Cool, boil out with water and filter.

(*a*) To a small portion of the filtrate add HNO_3 and $AgNO_3$.

A precipitate, **AgCl, AgBr** or **AgI,** indicates **Cl, Br** or **I.**

(*b*) In case a precipitate is obtained in (*a*), use the remainder of th tion to determine what members of the halogen group are present, acc to the methods outlined on page 299.

(5) **Phosphorus.** Boil a portion of the substance with conc. HNO_3 as the evolution of brown fumes indicates that oxidation is taking

DISCUSSION OF THE ANALYSIS OF ORGANIC SUBSTANCES.

The tests given in the regular analysis are tests for ions, or in a few cases, for free elements (Cl, Br, I, etc.). Since organic compounds do not generally ionize, they will not respond to these tests. In order to determine the constituents of these bodies, it is necessary to decompose them into substances which will readily ionize or substances for which definite tests are known. Thus, C, H, and P are recognized by their oxidation products, CO_2, H_2O, and H_3PO_4 Sulfur contained in organic compounds is changed to sodium sulfid which gives tests for the sulfid ion. Similarly the halogens heated with lime are changed into compounds which readily ionize.

The test for carbon and hydrogen depends upon the oxidation of the substance with copper oxid and the formation of CO_2 and water. Since all organic compounds contain carbon and practically all of them contain hydrogen, this test is of significance only as determining whether or not a substance is of organic nature.

The test for nitrogen depends upon the fact that whenever organic material containing both carbon and nitrogen is heated with an alkali metal, a cyanid is formed. When an alkali cyanid is boiled with a ferrous salt, potassium ferrocyanid is formed (see page 127), which with the ferric ion gives Prussian blue.

Free sulfur or sulfur contained in organic compounds, when heated with metallic sodium, forms sodium sulfid. According to the amount of sulfur present in the original substance, indications may be obtained with the various reagents mentioned. The test with the silver coin is more delicate than the other two and will indicate a trace of sulfur when no evidence would be obtained by the second or third tests. Sodium nitro-ferricyanid will respond to the presence of appreciable amounts of sulfur, while lead sulfid will not be precipitated except in the presence of considerable amounts of sodium sulfid due to a high percentage of sulfur in the original substance.

In the decomposition of the organic substance due to heating, any halogens present will unite with the lime to form calcium compounds, which will then give the ordinary tests for the halogen ions.

By heating with conc. nitric acid an organic substance may be completely oxidized, any phosphorus present being changed to phosphoric acid, which will give any of the regular tests.

APPENDIX

REAGENTS IN SOLUTION.

Acids.

				Volume to be diluted to 1 litre.
Hydrochloric, HCl, concentrated—				
	Sp. Gr. 1.190	37.2% HCl	12.1N	
	1.195	38.2	12.5N	
	1.200	39.1	12.9N	330 ccm. of 37.2% acid.
	dilute		4 N	
			4 N	320 ccm. of 38.2% acid.
			4 N	311 ccm. of 39.1% acid.
Nitric, HNO_3, concentrated—				
	Sp. Gr. 1.42	69.8% HNO_3	15.7N	
	dilute			254 ccm. of 69.8% acid.
Sulfuric, H_2SO_4, concentrated—				
	Sp. Gr. 1.839	95 % H_2SO_4	35.7N	
	1.840	95.6	36 N	
	1.841	97	36.5N	
	dilute		4 N	112 ccm. of 95 % acid.
			4 N	111 ccm. of 95.6% acid.
			4 N	110 ccm. of 97 % acid.
Acetic, $H(C_2H_3O_2)$, dilute			4 N	277 ccm. of 80 % acid.
Hydrofluoric, HF, concentrated, 40%				

Alkalies.

Ammonium hydroxid, NH_4OH, concentrated—				
	Sp. Gr. 0.90	28.3% NH_3	15 N	
		dilute	4 N	266 ccm. of 28.3% sol.

Alkalies (cont.):

		Grams of Substance in One Litre of Solution.§
Potassium hydroxid, KOH.	4 N	281

The material used for analytical purposes contains about 20% water. Hence the amount necessary for a solution four times normal is $(56.2 \times 4) \times 5/4 = 281$.

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§ Not in one litre of water. The substance should be dissolved in a quantity of distilled water sufficient for the purpose and the resulting solution then diluted to 1000 ccm. with distilled water.

Sodium hydroxid, NaOH. The material used for analytical purposes contains about 10% water. Hence the amount necessary for a solution four times normal is (40 × 4) × 10/9 = 177.7.	4 N	177

Other Reagents in Solution or in Liquid Form.

Alcohol—amyl		
—ethyl, or ordinary		
—methyl, or wood		
Aluminum chlorid, $AlCl_3.6H_2O$	N/2	40.3
—alum, $KAl(SO_4)_2.12H_2O$	N/2	79
Ammonium acetate, $NH_4(C_2H_3O_2)$	4 N	308
—carbonate, $(NH_4)_2CO_3$, (see page 318) about	4 N	192
—chlorid, NH_4Cl	4 N	214
—molybdate, $(NH_4)MoO_4$, (see page 318)	N	98
—oxalate, $(NH_4)_2C_2O_4.H_2O$, about	N/2	sat. sol.‡
—sulfid (colorless), $(NH_4)_2S$, (see page 318), about	4 N	
—polysulfid (yellow), $(NH_4)_2S \times S$, (see page 318)		
Aqua regia, (see page 43)		
Barium chlorid, $BaCl_2.2H_2O$	N	122.2
—hydroxid, $Ba(OH)_2.8H_2O$, about	N/3	sat. sol.‡
Bromin water, about	N/2	sat. sol.‡
Brucin, (see page 319)		
Calcium chlorid, $CaCl_2$	N	55.6
—hydroxid, $Ca(OH)_2$, "lime water," about	N/22	sat. sol.‡
—sulfate, $CaSO_4.2H_2O$, about	N/33	sat. sol.‡
Carbon disulfid, CS_2		
Chlorin water, about	N/5	sat. sol.
Chloroform		
Cobalt acetate, $Co(C_2H_3O_2).4H_2O$	N	124.5
—nitrate, $Co(NO_3)_2.6H_2O$	N	147.8
Ether		
Ferric chlorid, $FeCl_3$*	N	54.1
Iodin water, (see page 319), about	N/4	
Lead acetate, $Pb(C_2H_3O_2).3H_2O$*	N	189.5
"**Magnesia** mixture," (see page 319)	N	

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* Should contain a little free acid.

‡ Saturated solutions should be made by allowing the solvent to stand in contact with the solute for considerable time, the mixture being shaken occasionally. After settling thoroughly, the clear solution should be decanted or siphoned off into another bottle for use.

Manganese chlorid, $MnCl_2.4H_2O$, (see page 319)		
Mercuric chlorid, $HgCl_2$, about	N/2	sat. sol.[‡]
Mercurous nitrate, $(HgNO_3)_2$, (see page 319)	N/2	135.7
Phenylenediamin, (see page 319)		
Potassium chromate, K_2CrO_4	N	97.3
—cyanid, KCN	N	65.2
—dichromate, $K_2Cr_2O_7$	N	73.8
—ferricyanid, $K_3(Fe \equiv C_6N_6)$	N	109.8
—ferrocyanid, $K_4(Fe = C_6N_6)$	N	105.7
—iodid, KI	N	166.2
—nitrite, KNO_2	N	85.2
—permanganate, $KMnO_4$	N	79.1
—thiocyanate, KSCN	N	97.2
Silver nitrate, $AgNO_3$	N	169.9
Sodium acetate, $Na(C_2H_3O_2)$	4 N	328
—carbonate (dry), Na_2CO_3 or about	4 N	sat. sol.[‡]
—carbonate (crystals), $Na_2CO_3.10H_2O$	4 N	572
—nitroprussid, $Na_2(Fe \equiv C_5N_5NO).2H_2O$, 5 gr. in 100 ccm. H_2O		
—phosphate (acid), $Na_2HPO_4.12H_2O$	N	119
—stannite, Na_2SnO_2, (see foot-note, page 254)		
—sulfid, Na_2S, 10 gr. in 100 ccm. H_2O		
—sulfite, $Na_2SO_3.8H_2O$	N	135
Sodium thiosulfate, $Na_2S_2O_3.5H_2O$	N	124
Stannic chlorid, $SnCl_4$, (see page 319)	N/2	32.7
Stannous chlorid, $SnCl_2$, concentrated used in Bettendorff test for arsenious acid, (see page 319)		
—chlorid, $SnCl_2.2H_2O$, (see page 319)	N/2	56.5
Starch solution, (see page 319)		
—iodid solution, (see page 320)		
Sulfanilic acid mixture, (see page 320)		
Titanium sulfate, $Ti(SO_4)_2$, 10 grams to 100 ccm. H_2O		
Zinc acetate, $Zn(C_2H_3O_2)_2.7H_2O$	N	154.7

Salt Solutions.

luminum chlorid, $AlCl_3.6H_2O$	N/2	40.3
—nitrate, $Al(NO_3)_3.9H_2O$	N/2	62.5
—potassium sulfate, $KAl(SO_4)_2.12H_2O$	N/2	79

[‡] Saturated solutions should be made by allowing the solvent to stand in contact ith the solute for considerable time, the mixture being shaken occasionally. After ettling thoroughly, the clear solution should be decanted or siphoned off into another ottle for use.

Ammonium chlorid, NH_4Cl	N/2	26.8
—nitrate, NH_4NO_3	N/2	40
—sulfate, $(NH_4)_2SO_4$	N/2	33
Antimony trichlorid, $SbCl_3$, (see page 318)	N/2	37.6
—pentachlorid, $SbCl_3$, (see page 318)	N/2	29.8
Arsenic trichlorid, $AsCl_3$, (see page 318)	N/2	30.3
—pentachlorid, $AsCl_5$, (see page 318)	N/2	25.3
Barium chlorid, $BaCl_2.2H_2O$	N/2	61.1
—nitrate, $Ba(NO_3)_2$	N/2	65.4
Bismuth chlorid, $BiCl_3$, (see page 318)	N/2	52.5
—nitrate, $Bi(NO_3)_3.10H_2O$, (see page 319)	N/2	95.8
—sulfate, $Bi_2(SO_4)_3$, (see page 319)	N/2	57.9
Cadmium chlorid, $CdCl_2.2H_2O$	N/2	54.9
—nitrate, $Cd(NO_3)_2.4H_2O$	N/2	77.1
—sulfate $(CdSO_4)_3.8H_2O$	N/2	64.1
Calcium chlorid, $CaCl_2$	N/2	27.8
—nitrate, $Ca(NO_3)_2$	N/2	41
Chromium nitrate, $Cr(NO_3)_3.9H_2O$	N/2	66.7
—sulfate, $Cr_2(SO_4)_3.6H_2O$	N/2	41.7
—potassium sulfate, $KCr(SO_4)_2.12H_2O$	N/2	83.2
Cobalt acetate, $Co(C_2H_3O_2)_2.4H_2O$	N/2	62.3
—chlorid, $CoCl_2.6H_2O$	N/2	59.5
—nitrate, $Co(NO_3)_2.6H_2O$	N/2	72.7
—sulfate, $CoSO_4.7H_2O$	N/2	70.3
Copper chlorid, $CuCl_2.2H_2O$	N/2	42.6
—nitrate, $Cu(NO_3)_2.6H_2O$	N/2	73.9
—sulfate, $CuSO_4.5H_2O$*	N/2	62.4
Ferric chlorid, $FeCl_3$	N/2	27.1
—nitrate, $Fe(NO_3)_3.9H_2O$	N/2	67.3
—sulfate, $Fe_2(SO_4)_3.xH_2O$, about	N/2	84.7
Ferrous chlorid, $FeCl_2.4H_2O$	N/2	49.8
sulfate, $FeSO_4.7H_2O$*	N/2	69.5
Lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$*	N/2	94.8
—nitrate, $Pb(NO_3)_2$	N/2	82.8
Lithium chlorid, $LiCl$	N/2	21.3
—nitrate, $LiNO_3$	N/2	34.5
—sulfate, $LiSO_4$	N/2	27.5
Magnesium chlorid, $MgCl_2.6H_2O$	N/2	50.9
—nitrate, $Mg(NO_3)_2.6H_2O$	N/2	64.1
—sulfate, $MgSO_4.7H_2O$	N/2	61.6
Manganese chlorid, $MnCl_2.4H_2O$	N/2	49.5
—nitrate, $Mn(NO_3)_2.6H_2O$	N/2	71.8
—sulfate, $MnSO_4.4H_2O$	N/2	55.8
Mercuric chlorid, $HgCl_2$, about	N/2	sat. sol.‡

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* Should contain a little free acid.

‡ Saturated solutions should be made by allowing the solvent to stand in contact with the solute for considerable time, the mixture being shaken occasionally. After settling thoroughly, the clear solution should be decanted or siphoned off into another bottle for use.

—nitrate, $(Hg(NO_3)_2)_2.H_2O$*	N/2	83.3
Mercurous nitrate, $(HgNO_3)_2.2H_2O$, (see page 319)	N/2	135.5
Nickel chlorid, $NiCl_2.6H_2O$	N/2	59.5
—nitrate, $Ni(NO_3)_2.6H_2O$	N/2	72.7
—sulfate, $NiSO_4.7H_2O$	N/2	70.2
Potassium arsenate, K_2HAsO_4	N/2	36.4
—arsenite (meta), $KAsO_2$	N/2	24.4
—bromid, KBr	N/2	59.6
—chlorate, $KClO_3$, about	N/2	sat. sol.‡
—chlorid, KCl	N/2	37.3
—chromate, K_2CrO_4	N/2	48.7
Potassium cyanate, KOCN	N/2	40.6
—cyanid, KCN	N/2	32.6
—dichromate, $K_2Cr_2O_7$	N/2	36.9
—ferricyanid, $K_3(Fe\equiv C_6N_6)$	N/2	54.9
—ferrocyanid, $K_4(Fe=C_6N_6).3H_2O$	N/2	52.9
—fluorid, KF	N/2	29.1
—iodid, KI	N/2	83.1
—nitrate, KNO_3	N/2	50.6
—nitrite, KNO_2	N/2	42.6
—permanganate, $KMnO_4$	N/2	39.6
—sulfate, K_2SO_4	N/2	43.6
—sulfid, K_2S	N/2	27.6
—sulfite, $K_2SO_3.2H_2O$	N/2	48.6
—thiocyanate, KSCN	N/2	48.6
Silver nitrate, $AgNO_3$	N/2	84.9
Sodium acetate, $Na(C_2H_3O_2).3H_2O$	N/2	68
—arsenate, $Na_2HAsO_4.12H_2O$	N/2	67
—arsenite (meta), $NaAsO_2$	N/2	21.7
—borate (tetra), $Na_2B_4O_7.10H_2O$	N/2	15.9
—bromid, NaBr	N/2	51.5
—carbonate (dry), Na_2CO_3	N/2	26.5
—carbonate (crystals), $Na_2CO_3.10H_2O$	N/2	71.5
—chlorid, NaCl	N/2	29.3
—fluorid, NaF	N/2	21
—oxalate, $Na_2C_2O_4$	N/2	33.5
—phosphate (acid), $Na_2HPO_4.12H_2O$	N/2	59.5
—nitrate, $NaNO_3$	N/2	42.5
—nitrite, $NaNO_2$	N/2	34.5
—silicate, Na_2SiO_3	N/2	30.6
—silicofluorid, Na_2SiF_6, about	N/14	sat. sol.‡

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* Should contain some free acid.

‡ Saturated solutions should be made by allowing the solvent to stand in contact with the solute for considerable time, the mixture being shaken occasionally. After settling thoroughly, the clear solution should be decanted or siphoned off into another bottle for use.

Sodium sulfate, $Na_2SO_4.10H_2O$	N/2	80
—sulfid, Na_2S	N/2	19
—sulfite, $Na_2SO_3.8H_2O$	N/2	67
—tartrate, $Na_2(C_4H_4O_6).2H_2O$	N/2	57
—potassium tartrate, $NaK(C_4H_4O_6).4H_2O$	N/2	70
—thiosulfate, $Na_2S_2O_3.5H_2O$	N/2	62
Stannic chlorid, $SnCl_4$, (see page 319)	N/2	32
Stannous chlorid, $SnCl_2.2H_2O$, (see page 319)	N/2	56
Strontium chlorid, $SrCl_2$	N/2	39
—nitrate, $Sr(NO_3)_2.4H_2O$	N/2	70
Zinc chlorid, $ZnCl_2$	N/2	34
—nitrate, $Zn(NO_3)_2.6H_2O$	N/2	74
—sulfate, $ZnSO_4.7H_2O$	N/2	71

Reagents Requiring Special Methods of Preparation.

Ammonium carbonate. Dissolve 192 grams of the solid in 80 ccm. of con NH_4OH and 500 ccm. of water, and, after solution is complete, dilute to 1 lit with water.

Ammonium molybdate. Dilute 150 ccm. of conc. NH_4OH with an equ volume of water and dissolve in this mixture 72 grams of molybdic acid anh drid, MoO_3. Dilute 250 ccm. of conc. HNO_3 with twice its volume of water a pour the first solution slowly into the second solution, stirring constantly. All to stand in a warm place for a day or two, decant the clear liquid above a precipitate that may have formed and dilute to 1 litre.

Ammonium sulfid. Saturate a volume of conc. NH_4OH with H_2S by passi the gas into the liquid until it is no longer absorbed. Add a volume of con NH_4OH equal to the resulting solution and dilute with three volumes of wat

Ammonium polysulfid. "Yellow ammonium sulfid" is made by dissolvi about a gram of finely powdered sulfur in each litre of the above solution befo diluting it. After the sulfur has dissolved it may be diluted with an equal v ume of water.

Antimony pentachlorid. Dissolve 29.8 grams of $SbCl_5$ in 400 ccm. of con HCl mixed with an equal volume of water. After the solution is comple dilute to 1 litre. Or, dissolve 32 grams of Sb_2O_5 in 400 ccm. of conc. HCl mix with 400 ccm. of water and dilute to 1 litre.

Antimony trichlorid. Dissolve 37.6 grams of the crystals in 250 ccm. of con HCl mixed with an equal volume of water. After solution is complete dilute 1 litre.

Arsenic pentachlorid (?). Dissolve 36.4 grams of K_2HAsO_4 in water, add ccm. of conc. HCl and dilute to 1 litre.

Arsenic trichlorid. Dissolve 33 grams of As_2O_3 in 50 ccm. of conc. H diluted with 10 times its volume of water. When the oxid has entirely dissolv dilute to 1 litre. Or, dissolve 24.4 grams of $KAsO_2$ in water, add 50 ccm. conc. HCl and dilute to 1 litre.

Bismuth chlorid. Dissolve 52.5 grams of the crystals in 250 ccm. of wat to which 100 ccm. of conc. HCl has been added and dilute to 1 litre.

Bismuth nitrate. Dissolve 95.8 grams of $Bi(NO_3)_3.10H_2O$ or 50.8 grams of the "subnitrate," $BiNO_3(OH)_2$, in 250 ccm. of water mixed with 50 ccm. of conc. HNO_3. When solution is complete, dilute to 1 litre.

Bismuth sulfate. Dissolve 58.7 grams of the salt in 250 ccm. of water mixed with 25 ccm. conc. H_2SO_4 and, when solution is complete, dilute to 1 litre.

Brucin. Dissolve about 1 gram of the substance in 100 ccm. of conc. H_2SO_4.

Devarda's alloy. Fuse together in a covered earthenware crucible 450 grams of aluminum, 50 grams of zinc and 500 grams of copper. After the mixture has become liquid, pour out upon a cold surface and pulverize when cold.

Iodin water. Dissolve 50 grams of KI in a litre of water and saturate with iodin by allowing the solution to stand in contact with an excess of iodin crystals for some time with occasional shaking. Afterwards decant the clear dark-brown solution.

"Magnesia mixture." Dissolve 101.8 grams of $MgCl_2.6H_2O$ and 107 grams NH_4Cl in water, add 400 ccm. conc. NH_4OH and dilute to 1 litre.

Manganese chlorid (concentrated). Saturate conc. HCl with the crystallized salt, $MnCl_2.4H_2O$.

Mercurous nitrate. Dissolve 135.5 grams of the crystallized salt in a half litre of water to which 25 ccm. of conc. HNO_3 has been added. Dilute to 1 litre and add 50–100 grams of mercury. Or, treat 100 grams of mercury with 25 ccm. of conc. HNO_3 diluted to 125 ccm. with water and maintain near the boiling temperature until the metal has disappeared, adding more acid in small amounts if necessary. Decant the clear liquid and add 50–100 grams of mercury and dilute to 1 litre.

Phenylenediamin (meta). Dissolve 2–3 grams of the solid in 10 ccm. of conc. HCl and 90 ccm. of water.

Potassioscope Liquid. Dissolve about 0.5 gram of Gentian Blue in a litre of 95 per cent. alcohol. Place in well-corked flat bottles of such size that a layer of solution about 1 inch thick may be obtained. Six ounce vials are satisfactory. Bottles with curved surfaces should be avoided.

A solution of the dye in dilute alcohol will precipitate on standing.

Stannous chlorid (concentrated for Bettendorff test for arsenious acid). Treat 600 grams of granulated tin with a litre of conc. HCl and maintain the mixture at a temperature sufficiently high to keep up a vigorous action of the acid on the metal. When hydrogen is no longer liberated, decant the solution and add a few ccm. of conc. HCl and a few pieces of the metal to the bottle in which it is to be kept. Or, if only a small amount of the reagent is desired, dissolve 113 grams of $SnCl_2.2H_2O$ in 75 ccm. of conc. HCl and add a few pieces of the metal.

Stannous chlorid (general reagent). Dilute 50 ccm. of the previous solution with an equal volume of conc. HCl and dilute to 1 litre with water, keeping a few pieces of metallic tin in contact with the solution.

Stannic chlorid. Add bromin water to 50 ccm. of the concentrated solution of $SnCl_2$ prepared as above until a permanent yellow color is produced. Boil off the excess of bromin (indicated by disappearance of color) and dilute to 1 litre.

Starch solution. Finely pulverize 1 gram of starch, rub up to a thin mixture with about 10 ccm. water and pour immediately into 100 ccm. of boiling water. Boil for 5–10 minutes.

Starch-iodid mixture. Add 1 gram of KI to 100 ccm. of the starch solution prepared as previously directed.

Sulfanilic acid mixture. Dissolve 0.5 gram of sulfanilic acid in 150 ccm. of dilute acetic acid made by mixing 50 ccm. of the 80 per cent. acid with 100 ccm. of water. Boil 0.1 gram of α-naphthylamin with 25 ccm. of water and decant the colorless solution from the violet residue and add 50 ccm. of dilute acetic acid of the strength given to the solution.

The two solutions are then mixed and should be nearly colorless. If a pink tinge should appear on standing, it should be removed by shaking the solution with zinc dust and then filtering. Use 1 ccm. in testing for nitrous acid.

Sulfuric acid. Since a large amount of heat is produced when conc. H_2SO_4 is diluted, to avoid dangerous spattering and breaking of containers, the conc. acid should always be added to the necessary volume of water slowly and with constant stirring.

REAGENTS IN SOLID FORM.

Ammonium chlorid, NH_4Cl.
—nitrate, NH_4NO_3.
Barium hydroxid, $Ba(OH)_2.8H_2O$.
Borax, $Na_2B_4O_7.10H_2O$.
Calcium carbonate, $CaCO_3$.
—fluorid, CaF_2 (fluorspar).
—hydroxid, $Ca(OH)_2$, "slacked lime."
—oxid, CaO, lime.
Copper, foil.
—oxid, CuO.
Devarda's alloy (see page 319).
Ferrous sulfate, $FeSO_4.7H_2O$.
Iron filings.
—nails.
Lead dioxid, PbO_2.
Lime (see calcium oxid).
Litmus paper.
Microcosmic salt, $HNa(NH_4)PO_4.4H_2O$.
Paraffine.
Potassium carbonate, K_2CO_3.
—chlorate, $KClO_3$.
—cyanid, KCN.
—dichromate, $K_2Cr_2O_7$.
—ferricyanid, $K_3(Fe\equiv C_6N_6)$.
—nitrate, KNO_3.
—sulfate (acid), $KHSO_4$.
Sodium, metal.
—carbonate, Na_2CO_3.
—carbonate (acid), $NaHCO_3$.
—and potassium carbonate mixture for fusions.
—hydroxid, NaOH.
—meta-phosphate, $NaPO_3$ (prepared from microcosmic salt) (see page 78).
—peroxid, Na_2O_2.
—sulfite, $Na_2SO_3.8H_2O$.
Sulfur, powdered.
Tumeric paper.
Zinc, dust.
—metal.

SPECIFIC GRAVITY OF SOLUTIONS AT 15° C.

SULFURIC ACID. (*Lunge and Isler.*)

Specific Gravity.	Per Cent. H_2SO_4.	Specific Gravity.	Per Cent. H_2SO_4.	Specific Gravity.	Per Cent. H_2SO_4.
1.000	0.09	1.320	41.50	1.640	71.99
1.010	1.57	1.330	42.66	1.650	72.88
1.020	3.03	1.340	43.74	1.660	73.64
1.030	4.49	1.350	44.82	1.670	74.51
1.040	5.96	1.360	45.88	1.680	75.42
1.050	7.37	1.370	46.94	1.690	76.30
1.060	8.77	1.380	48.00	1.700	77.17
1.070	10.19	1.390	49.06	1.710	78.01
1.080	11.60	1.400	50.11	1.720	78.92
1.090	12.99	1.410	51.15	1.730	79.80
1.100	14.35	1.420	52.15	1.740	80.68
1.110	15.71	1.430	53.11	1.750	81.56
1.120	17.01	1.440	54.07	1.760	82.44
1.130	18.31	1.450	55.03	1.770	83.32
1.140	19.61	1.460	55.97	1.780	84.50
1.150	20.91	1.470	56.90	1.790	85.70
1.160	22.19	1.480	57.83	1.800	86.90
1.170	23.47	1.490	58.74	1.810	88.30
1.180	24.76	1.500	59.70	1.820	90.05
1.190	26.04	1.510	60.65	1.825	91.00
1.200	27.32	1.520	61.59	1.830	92.10
1.210	28.58	1.530	62.53	1.834	93.05
1.220	29.84	1.540	63.43	1.837	94.20
1.230	31.11	1.550	64.26	1.839	95.00
1.240	32.28	1.560	65.08	1.840	95.60
1.250	33.40	1.570	65.90	1.841	97.00
1.260	34.57	1.580	66.71	1.8415	98.20
1.270	35.71	1.590	67.59	1.841	98.70
1.280	36.87	1.600	68.51	1.840	99.20
1.290	38.03	1.610	69.43	1.839	99.70
1.300	39.19	1.620	70.32		
1.310	40.35	1.630	71.16		

HYDROCHLORIC ACID. (*Lunge and Marchlewski.*)

Specific Gravity.	Per Cent. HCl.	Specific Gravity.	Per Cent. HCl.	Specific Gravity.	Per Cent. HCl.
1.000	0.16	1.070	14.17	1.140	27.66
1.005	1.15	1.075	15.16	1.145	28.61
1.010	2.14	1.080	16.15	1.150	29.57
1.015	3.12	1.085	17.13	1.155	30.55
1.020	4.13	1.090	18.11	1.160	31.52
1.025	5.15	1.095	19.06	1.165	32.49
1.030	6.15	1.100	20.01	1.170	33.46
1.035	7.15	1.105	20.97	1.175	34.42
1.040	8.16	1.110	21.92	1.180	35.39
1.045	9.16	1.115	22.86	1.185	36.31
1.050	10.17	1.120	23.82	1.190	37.23
1.055	11.18	1.125	24.78	1.195	38.16
1.060	12.19	1.130	25.75	1.200	39.11
1.065	13.19	1.135	26.70		

NITRIC ACID. (*Lunge and Rey.*)

Specific Gravity.	Per Cent. HNO_3.	Specific Gravity.	Per Cent. HNO_3.	Specific Gravity.	Per Cent. HNO_3.
1.00	0.00	1.18	29.38	1.36	57.57
1.01	1.90	1.19	30.88	1.37	59.39
1.02	3.70	1.20	32.36	1.38	61.27
1.03	5.50	1.21	33.82	1.39	63.23
1.04	7.26	1.22	35.28	1.40	65.30
1.05	8.99	1.23	36.78	1.41	67.50
1.06	10.68	1.24	38.29	1.42	69.80
1.07	12.33	1.25	39.82	1.43	72.17
1.08	13.95	1.26	41.34	1.44	74.68
1.09	15.53	1.27	42.87	1.45	77.28
1.10	17.11	1.28	44.41	1.46	79.98
1.11	18.67	1.29	45.95	1.47	82.90
1.12	20.23	1.30	47.49	1.48	86.05
1.13	21.77	1.31	49.07	1.49	89.60
1.14	23.31	1.32	50.71	1.50	94.09
1.15	24.84	1.33	52.37	1.51	98.10
1.16	26.36	1.34	54.07	1.52	99.67
1.17	27.88	1.35	55.79		

AMMONIA SOLUTIONS. (*Lunge and Wiernick.*)

Specific Gravity.	Per Cent. NH_3.	Specific Gravity.	Per Cent. NH_3.	Specific Gravity.	Per Cent. NH_3.
0.882	34.95	0.922	21.12	0.962	9.35
0.884	34.10	0.924	20.49	0.964	8.84
0.886	33.25	0.926	19.87	0.966	8.33
0.888	32.50	0.928	19.25	0.968	7.82
0.890	31.75	0.930	18.64	0.970	7.31
0.892	31.05	0.932	18.03	0.972	6.80
0.894	30.37	0.934	17.42	0.974	6.30
0.896	29.69	0.936	16.82	0.976	5.80
0.898	29.01	0.938	16.22	0.978	5.30
0.900	28.33	0.940	15.63	0.980	4.80
0.902	27.65	0.942	15.04	0.982	4.30
0.904	26.98	0.944	14.46	0.984	3.80
0.906	26.31	0.946	13.88	0.986	3.30
0.908	25.65	0.948	13.31	0.988	2.80
0.910	24.99	0.950	12.74	0.990	2.31
0.912	24.33	0.952	12.17	0.992	1.84
0.914	23.68	0.954	11.60	0.994	1.37
0.916	23.03	0.956	11.03	0.996	0.91
0.918	22.39	0.958	10.47	0.998	0.45
0.920	21.75	0.960	9.91	1.000	0.00

LIST OF ELEMENTS.* 1906.

Name.	Symbol.	Valences.	At.Wt.	Name.	Symbol.	Valences.	At.Wt.
Aluminum	Al	3	27.1	Neon	Ne	0	20
Antimony	Sb	3–5	120.2	**Nickel**	Ni	2–3	58.7
Argon	A	0	39.9	Niobium	Nb	5–3	94
Arsenic	As	3–5	75	**Nitrogen**	N	5–3	14
Barium	Ba	2	137.4	Osmium	Os	8–6–4	191
Beryllium	Be	2	9.1	**Oxygen**	O	2	16
Bismuth	Bi	3	208.5	Palladium	Pd	4–2	106.5
Boron	B	3	11	**Phosphorus**	P	5–3	31
Bromin	Br	1–5	80	**Platinum**	Pt	4–2	194.8
Cadmium	Cd	2	112.4	**Potassium**	K	1	39.2
Cæsium	Cs	1	132.9	Praseodymium	Pr	3	140.5
Calcium	Ca	2	40.1	Radium	Ra	2	225
Carbon	C	4–2	12	Rhodium	Rh	3	103
Cerium	Ce	4–3	140.2	Rubidium	Rb	1	85.5
Chlorin	Cl	1–5–7–3	35.5	Ruthenium	Ru	4–3–6–8	101.7
Chromium	Cr	3–6–7–2	52.1	Samarium	Sa	3	150.3
Cobalt	Co	2–3	59	Scandium	Sc	3	44.1
Copper	Cu	2–1	63.6	Selenium	Se	2–6–4	79.2
Erbium	Er	3	166	**Silicon**	Si	4	28.4
Fluorin	F	1	19	**Silver**	Ag	1	107.9
Gadolinium	Gd	3	156	**Sodium**	Na	1	23
Gallium	Ga	3	70	**Strontium**	Sr	2	87.6
Germanium	Ge	4–2	72.5	**Sulfur**	S	2–4–6	32.1
Gold	Au	1–3	197.2	Tantalum	Ta	5	183
Helium	He	0	4	Tellurium	Te	2–4–6	127.6
Hydrogen	H	1	1	Terbium	Tb	3	160
Indium	In	3	115	Thallium	Tl	1–3	204.1
Iodin	I	1–5–7	127	Thorium	Th	4–3	232.5
Iridium	Ir	3–4–2	193	Thullium	Tu	3	171
Iron	Fe	3–2	55.9	**Tin**	Sn	2–4	119
Krypton	Kr	0	81.8	Titanium	Ti	4	48.1
Lanthanum	La	3	138.9	Tungsten	W	6–4–2	184
Lead	Pb	2–4	206.9	Uranium	U	6–4	238.5
Lithium	Li	1	7	Vanadium	V	5–3	51.2
Magnesium	Mg	2	24.4	Xenon	Xe	0	128
Manganese	Mn	2–7–4–6–3	55	Ytterbium	Yb	3	173
Mercury	Hg	2–1	200	Yttrium	Y	3	89
Molybdenum	Mo	6–4–2	96	**Zinc**	Zn	2	65.4
Neodymium	Nd	3	143.6	Zirconium	Zr	4	90.6

NOMENCLATURE.

The elements are named quite arbitrarily, except that the ending "ium" or "um" is used to designated the possession of metallic properties. All of the more recently-named metals are so indicated. Very often an element is named because of some very characteristic property, the name being derived usually from Greek words signifying the possession of this quality. Chlorin and iodin come from the Greek words meaning "green" and "violet," both of these names signifying the color of the vapor of these elements. Bromin is from the word meaning "stench," referring to the manner in which this substance affects the membranes of the nose and throat. Hydrogen, oxygen and nitrogen are compounded from the verb gennao, meaning "to produce," and from the nouns meaning "water," "acid," and "nitre," respectively. Hydrogen is the element which forms water when it burns; oxygen is a constituent of very many acids, once thought to be present in all, and nitrogen a principal component of nitre. Potassium, sodium and aluminum are the metals present in potash, soda and alum. Phosphorus is compounded from Greek words, and means "the light-bearer," referring to the phosphorescence of the element. Chromium is from the word meaning color, suggesting the fact that most compounds of this element are highly colored. Certain of the elements are named from the countries in which they were discovered, as magnesium from Magnesia; scandium from Scandanavia; gallium from Gaul, the older name for France; germanium from Germany. Tellurium comes from the Greek word meaning the earth, selenium, similarly, signifies the moon, and helium the sun, the latter name being given because of the fact that this element was known to exist in the sun before it was discovered on earth. Gold, silver, copper, lead, mercury, tin and iron were known to the ancients, and in their chemical symbols the older names are still retained.

---

* Calculated from the basis, O = 16.

In the naming of chemical compounds, however, certain definite rules are followed. All binary compounds (*i. e.*, consisting of two substances) are designated by naming the metallic element first followed by the stem of the non-metallic element to which the suffix, "id," is added, as HCl, hydrogen chlorid; ZnS, zinc sulfid; CaO, calcium oxid; Na(OH), sodium hydroxid, the hydroxyl radicle being considered as a unit.

If two bodies are composed of the same elements in different proportions, the one containing the greater proportion of the non-metallic constituent is designated by the ending "ic," while the compound with the smaller proportion of the non-metallic constituent is indicated by the suffix "ous." Thus $FeCl_3$ is ferric chlorid; $FeCl_2$, ferrous chlorid; SnO_2, stannic oxid; SnO, stannous oxid; H_2SO_4, sulfuric acid; H_2SO_3. sulfurous acid.

When more than two compounds containing the same elements exist, they are designated by the prefixes, "per," meaning "higher," and "hypo," meaning "lower."

Salts of acids ending in "ous" are indicated by the ending "ite" while salts of "ic" acids end in "ate."

The following table will make plain the usage:

Formula.	Acid.	Salt.	Formula.
HClO	**Hypo**chlor**ous** acid	Sodium **hypo**chlor**ite**	NaClO
$HClO_2$	Chlor**ous** acid	Sodium chlor**ite**	$NaClO_2$
$HClO_3$	Chlor**ic** acid	Sodium chlor**ate**	$NaClO_3$
$HClO_4$	**Per**chlor**ic** acid	Sodium **per**chlor**ate**	$NaClO_4$

PHYSICAL PROPERTIES OF THE ELEMENTS.

Element.	Specific Gravity.	Melting Point.	Boiling Point.	Element.	Specific Gravity.	Melting Point.
Aluminum	2.67	657	1470–1700	Neon		
Antimony	6.72	432	1500–1700	Nickel	8.85	1484
Argon		—187.9	—186.1	Niobium	7.06	1950
Arsenic	5.70	500	449.5	Nitrogen		—214
Barium		850	950	Osmium	22.48	2500
Beryllium	1.85	>960		Oxygen		>—230
Bismuth	9.65	269	1435	Palladium	11.40	1586
Boron	2.58	Infusible	3500	Phosphorus	1.82 Y 2.11 R	44.2
Bromin	3.10	—7.3	63	Platinum	21.48	1770
Cadmium	8.72	321.7	778	Potassium	0.87	62.5
Caesium	1.88	26.37	670	Praseodymium		940
Calcium		780		Radium		
Carbon	3.55 D 2.25 G 1.70 A	3500		Rhodium	11.50	2000
Cerium	6.65	623		Rubidium	1.52	38.5
Chlorin		—102	—33.6	Ruthenium	11.20	1900
Chromium	6.47	1515		Samarium		
Cobalt	8.55	1530		Scandium		
Copper	8.93	1045	2100	Selenium	4.48	175
Erbium				Silicon	2.49	1200
Fluorin		—223	—187	Silver	10.50	955
Gadolinium				Sodium	0.97	95.6
Gallium	5.95	30.15		Strontium	2.55	900
Germanium	5.47	900	1350	Sulfur	2.06 O 1.96 M	115–119
Gold	19.32	1065		Tantalum	10.70	2250
Helium		>—271	—267	Tellurium	6.24	446
Hydrogen		—256.5	—252.5	Terbium		
Indium	7.40	155	800	Thallium	11.85	302
Iodin	4.95	1142	184.4	Thorium	11.00	
Iridium	21.83	1950		Thullium		
Iron	7.80	1804		Tin	7.29	232
Krypton		—169	—151.7	Titanium		3000
Lanthanum	6.10	810		Tungsten	17.20	1700
Lead	11.37	327	1400–1600	Uranium	18.68	800
Lithium	0.59	186	< 1400	Vanadium	5.50	1630
Magnesium	1.75	632.6	1100	Xenon		—140
Manganese	7.25	1900		Ytterbium		
Mercury	13.57	—38.85	357	Yttrium		
Molybdenum	8.65			Zinc	7.15	419
Neodymium		840		Zirconium	4.15	1500

POTENTIAL SERIES.

The following list shows the comparative readiness with which various metals tend to take on charges of plus electricity and pass into the ionic condition, the element possessing this property in the maximum degree standing first. Every metal in this list is said to be *positive* to all the metals below it, *i. e.,* tends to pass more readily into the ionic condition, or liberates more energy in taking on the electrical charge. Since this determines the potential when two metals are joined together in a cell, this arrangement is known as the Potential Series.

Because each element tends to pass more readily into the ionic condition than any element standing lower in the series, whenever a metal is introduced into a solution of a salt of another metal, theoretically, the more positive metal should replace the less positive, the former should take the charge from the latter, the more positive dissolving as the less positive is precipitated from solution. Under appropriate condition this can generally be accomplished in most cases but the action is most vigorous between metals widely separated in the Potential Series. For the same reason, those metals standing higher than hydrogen dissolve readily in acids unless an insoluble product forming a protective coating about the metal is produced by the reaction. On the other hand, those metals standing lower than hydrogen in this series are not readily attacked by acids when the action is due to hydrogen ions only. (See footnote, page 17.)

1 Potassium
2 Sodium
3 Lithium
4 Barium
5 Strontium
6 Calcium
7 Magnesium
8 Aluminum
9 Manganese
10 Zinc
11 Cadmium
12 Iron
13 Cobalt
14 Nickel
15 Lead
16 Hydrogen
17 Bismuth
18 Arsenic
19 Antimony
20 Tin
21 Copper
22 Mercury
23 Silver
24 Platinum
25 Gold

Few non-metallic elements form simple anions. The following order has been determined, however, among those that are well known:

1 Fluorin
2 Chlorin
3 Bromin
4 Oxygen
5 Iodin
6 Sulfur

METRIC MEASURES WITH ENGLISH EQUIVALEN

Measures of Length.

1 Millimeter, mm. = .03937 inches.
1 Centimeter, cm. = 10 mm. = .3937 inches.
1 Decimeter, dm. = 10 cm. = 3.9371 inches.
1 Meter, m. = 10 dm. = 39.3708 inches.
1 Kilometer, km. = 1000 m. = .6214 miles.

Measures of Volume.

1 Cubic centimeter, ccm. = .06103 cubic inch
1 Cubic decimeter, (liter), l. = 1000 ccm. = { 61.027 cubic inches, 1.057 U. S. quarts.
1 Cubic meter = 1000 l. = 35.3166 cubic feet.

Measures of Weight.

1 Milligram, mg. = .0154 grains.
1 Gram = 1000 mg. = 15.432 grains.
1 Kilogram (kilo) = 1000 grams. = 2.2046 pounds av.

ENGLISH MEASURES WITH METRIC EQUIVALEN

1 Inch = 25.399 millimeters.
1 Foot = .3048 meters.
1 Mile = 1.609 kilometers.

1 Cubic inch = 16.386 cubic centim
1 Cubic foot = 28.315 liters.
1 Quart = .9463 liters.

1 Grain = .0648 grams.
1 Ounce av. = 28.3496 grams.
1 Pound av. = .4536 kilograms.

CONVERSION FACTORS.

TO CHANGE	TO	MULTIPLY BY
Inches	Centimeters	2.54
Feet	Meters	.305
Miles	Kilometers	1.609
Meters	Inches	39.37
Kilometers	Miles	.621
Square inches	Square centimeters	6.452
Square yards	Square meters	.836
Square centimeters	Square inches	.155
Square meters	Square yards	1.196
Cubic inches	Cubic centimeters	16.386
Cubic yards	Cubic meters	.765
Cubic centimeters	Cubic inches	.061
Cubic meters	Cubic yards	1.308
Fluid ounces	Cubic centimeters	29.57
Quarts	Liters	.946
Cubic centimeters	Fluid ounces	.034
Liters	Quarts	1.057
Grains	Milligrams	64.799
Ounces (av.)	Grams	28.35
Pounds (av.)	Kilograms	.454
Ounces (troy)	Grams	31.103
Pounds (troy)	Kilograms	.373
Grams	Grains	15.432
Kilograms	Pounds	2.205

TABLE OF SOLUBILITIES.

	−OH	=O	=S	−F	−Cl	−Br	−I	−CN	−OCN	−SCN	(Fe = C$_6$N$_6$) ≡	(Fe = C$_6$N$_6$) ≡	−NO$_2$	−NO$_3$	−ClO
Na —	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
K —	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
NH$_4$ —	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mg =	3	3	1	4	1	1	1	1	1	1	1	1	1	1	1
Ca =	2	1	2	4	1	1	1	1	1	1	1	1	1	1	1
Sr =	2	1	1–2	4	1	1	1	1	1	1	1	1	1	1	1
Ba =	1	1	1	4	1	1	1	2	1	1	1	1	1	1	1
Zn =	3	3	3	3	1	1	1	3	3	1	3	3	—	1	—
Mn =	3	3	3	3	1	1	1	3	3	1	4	3	—	1	—
Ni =	3	3	4	2	1	1	1	4	3	1	4	4	—	1	—
Co =	3	3	4	2	1	1	1	4	3	1	4	4	—	1	—
Fe =	3	3	3	2	1	1	1	4	3	1	4	4	—	1	—
Fe ≡	3	4	—	1	1	1	1	*a*	*a*	1	1	4	—	1	—
Cr ≡	3	4	—	1	1	1	1	*a*	*a*	1	—	—	—	1	—
Al ≡	3	4	—	1	1	1	1	*a*	*a*	1	—	*a*	—	1	—
Sn =	3	3	3	1	1	1	2	*a*	*a*	—	3	3	—	—	—
Sn ≡	3	4	3	1	1	1	1	*a*	*a*	—	3	3	—	—	—
Sb ≡	3	3	3	1	1*b*	1*b*	1*b*	—	—	—	—	—	—	—	—
As ≡	2	2	4	1	1	1	1	—	—	—	—	—	—	—	—
Cd =	3	3	3	2	1	1	1	3	3	1	3	3	—	1	—
Cu =	3	3	3	3	1	1	4	4	3	3	4	4	—	1	—
Bi ≡	3	3	3	1	1*b*	1	1	*a*	—	1	3	3	—	1	—
Pb =	3	3	3	3	2–4	2–4	2–4	3	3	1	3	3	—	1	—
Hg =	—	3	4	1	1	1	2	1	1	2–3	3	1	—	1	—
Hg —	—	—	—	3	4	4	2	—	3	3	4	4	—	1	—
Ag —	—	3	3	1	5	5	5	5	3	4	3	4	2	1	1

— = Unknown, rare, or not readily formed. 1 = Readily soluble in wa
2 = Sparingly soluble in water; generally dissolve readily in very dilute acids. 3
Practically insoluble in water, but dissolve readily in 4N mineral acids. 4 = Requ
hot, strong acids for appreciable solvent effect. 5 = Practically insoluble in aci

a = Hydroxid is precipitated. *b* = Insoluble basic salt likely to form.

TABLE OF SOLUBILITIES.

$-ClO_4$	$-MnO_4$	$=SO_3$	$=S_2O_3$	$=SO_4$	$=CrO_4$	$=SiO_3$	$=CO_3$	$=C_2O_4$	$=C_4H\,O_6$	$-C_2H_3O_2$	$\equiv PO_4$	$\equiv AsO_4$	$\equiv AsO_3$	$\equiv BO_3$	$=SiF_6$	
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	$-Na$
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2–4	$-K$
1	1	1	1	1	1	—	1	1	1	1	1	1	1	1	1	$-NH_4$
1	1	2	1	1	1	3	3	2	3	1	3	3	3	2	1	$=Mg$
1	1	3	1	2–4	1	3	3	3	3	1	3	3	3	2	1	$=Ca$
1	1	3	1	5	2	3	3	3	3	1	3	3	3	2	1	$=Sr$
1	1	3	2	5	3	3	3	3	3	1	3	3	3	2	2–4	$=Ba$
1	1	2	1	1	1	3	3	3	3	1	3	3	3	2	1	$=Zn$
1	1	2	1	1	1	3	3	2	3	1	3	3	3	2	1	$=Mn$
1	1	3	1	1	3	3	3	3	3	1	3	3	3	3	1	$=Ni$
1	1	3	1	1	3	3	3	3	3	1	3	3	3	3	1	$=Co$
1	—	2	1	1	—	3	3	3	3	1	3	3	3	3	1	$=Fe$
1	1	1	1	1	—	3	*a*	3	1	1	3	3	3	3	—	$\equiv Fe$
—	—	1	1	1	—	3	*a*	2	1	1	3	3	3	3	—	$\equiv Cr$
1	—	1	1	1	—	3	*a*	3	1	1	3	3	3	2	—	$\equiv Al$
—	—	3	1	1	3	—	*a*	3	3	1*b*	3	3	—	3	1	$=Sn$
—	—	—	—	—	—	—	*a*	—	—	—	3	3	—	—	—	≣Sn
—	—	—	—	2	3	—	—	3	3	—	—	3	3	—	—	$\equiv Sb$
—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—	$\equiv As$
1	1	3	1	1	1	3	3	3	3	1	3	3	3	3	1	$=Cd$
1	1	3	1	1	3	3	3	3	3	1	3	3	3	3	1	$=Cu$
2	—	3	1	1	3	3	3	3	3	1	3	3	3	3	1	$\equiv Bi$
1	1	3	2	4	3	3	3	3	3	1	3	3	3	3	1	$=Pb$
1	—	—	—	1	2	3	—	3	2	1	3	3	3	3	1	$=Hg$
1	—	—	—	3	3	—	—	3	3	1	3	3	3	3	1	$-Hg$
1	2	3	2	2	3	3	3	3	3	1	3	3	3	3	1	$-Ag$

— = Unknown, rare, or not readily formed. 1 = Readily soluble in water. 2 = Sparingly soluble in water; generally dissolve readily in very dilute acids. 3 = Practically insoluble in water, but dissolve readily in 4N mineral acids. 4 = Require hot, strong acids for appreciable solvent effect. 5 = Practically insoluble in acids.

a = Hydroxid is precipitated. *b* = Insoluble basic salt likely to form.

50
75
25

9)750
83

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NOTE:—*f* indicates frontispiece.

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